Jatropha seed cake valorization for non-food applications

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Didedikasikan untuk istriku Rohmah, dan anak-anakku
Mala, Firda, Qowam, Tia, dan Miqdad

Table of content

Chapter 1

Inroduction

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Abstract

This chapter provides an overview on global developments in energy generation and transportation fuels. The use of biomass as an alternative for fossil resources is discussed followed by an introduction on the potential of *Jatropha curcas* L. (JCL) plant oil for biodiesel production. The current and future energy resources and consumption in Indonesia will be reported, along with Indonesia's energy policy and the status of JCL development in Indonesia. Valorization concepts for the seed cake after pure plant oil isolation and plant parts other than the oil seeds will be introduced. Finally, an outline of this thesis is provided.

1.1. Global developments in energy and transportation fuels

The global energy consumption has grown exponentially in the last century. This growth has been driven by two main factors, i) an increase in world population, which already exceeds 7 billion and ii) an ongoing increase in welfare levels [1]. The annual global primary energy consumption in 2010 grew by 5.6% to 12002 Mtoe (megatons of oil equivalent), the strongest growth since 1973. The main resources for primary energy generation are predominantly from fossil origin, examples are crude oil (33.6%), coal (29.6%), and natural gas (23.8%) [2]. The International Energy Agency (IEA) predicts that the global energy consumption will increase by one-third in the period 2010-2035. As a consequence, CO_2 emissions will increase from 30.4 Gt (gigatons) to 36.4 Gt between 2010 and 2035 [3], which is expected to have a major impact on the global climate [4].

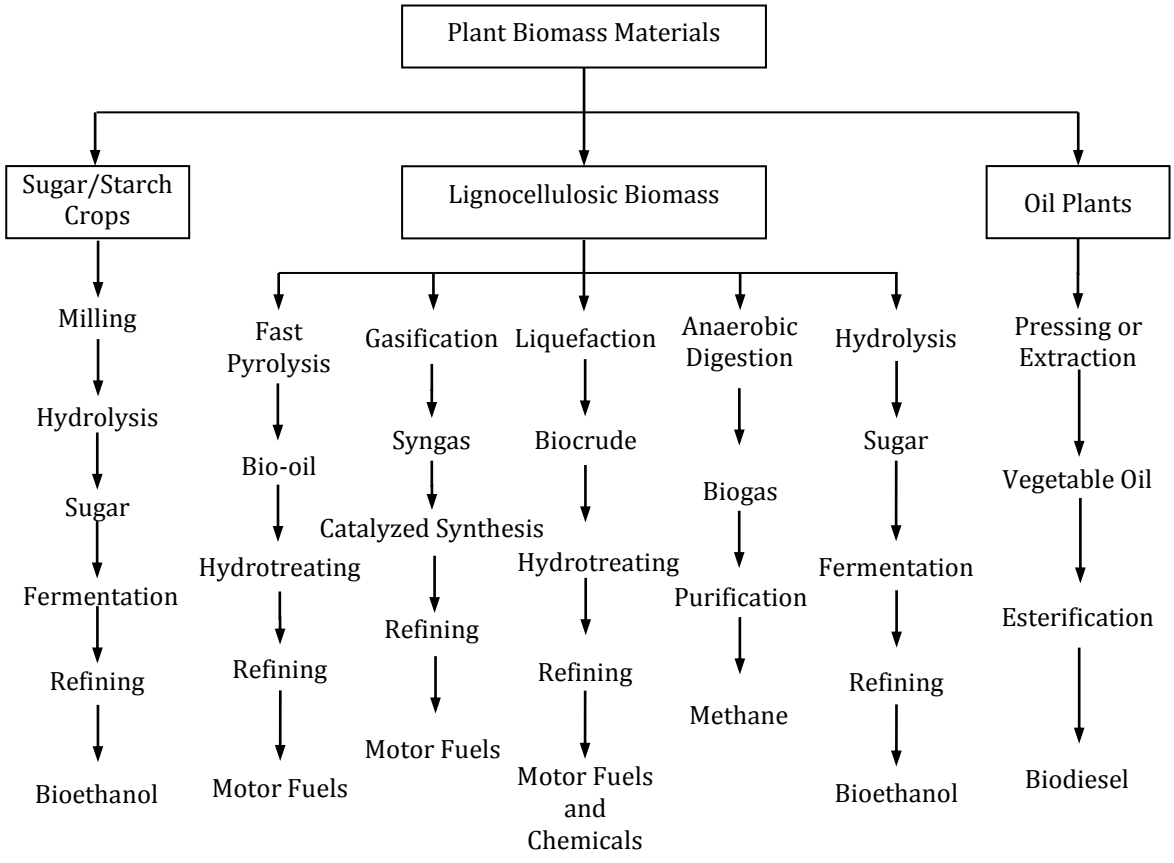

Figure 1. Overview of conversion processes for plant materials into biofuels [5]

Therefore, the quest for sustainable and environmentally benign alternatives for fossil resources is actively pursued. Well known examples are wind, solar, geothermal, marine, biomass and hydro, for which the total demand is expected to grow from 860 Mtoe in 2009 to 2365 Mtoe in 2035. As a consequence, the share of renewable energy in the primary energy mix will increase from 7% in 2009 to 14% in 2035 [3].

Wind, solar, geothermal, marine and hydro are excellent alternatives for fossil fuels used in power and heat generation. Biomass resources, however, are the only sources of renewable carbon and as such are suitable for biofuels production to replace gasoline, diesel and jet fuel in the transportation sector. For short distance transport, the use of green electricity may be convenient, though it is not an option in the aviation sector and in heavy long distance transport.

Biofuels refer to solid, liquid or gaseous fuels produced from plant biomass. A wide range of technologies for biofuels production have been developed, see Figure 1 for details.

Table 1. Classification of biofuels based on their production technologies

Generation	Feedstock	Example
First generation biofuels	Sugar, starch, vegetable oils, animal fats	Bioethanol, vegetable oil, biodiesel, biogas
Second generation biofuels	Non-food crops, wheat straw, corn, wood, solid waste, energy crop	Bioethanol, pyrolysis oils, bio-DME, biohydrogen, FT-diesel
Third generation biofuels	Algae	Vegetable oil, biodiesel

DME: dimethyl ether; FT: Fischer Tropsch

Biofuels can be classified into generations and three generations are now widely used, see Table 1 for details [5]**.** First generation biofuels are made from sugar, starch, vegetable oils, or animal fats. These biofuels have been commercialized and the products are available on the market. Examples are sugarcane ethanol in Brazil, corn ethanol in the US, rape seed biodiesel in Europe and palm oil biodiesel in Malaysia and Indonesia [5-7]. Biodiesel, also known as FAME (fatty acid methyl esters) is typically produced by a transesterification reaction of plant oil with methanol. The reaction is very versatile and a wide range of oils and alcohols can be used. Most frequently methanol is used though higher alcohols like ethanol, 2-propanol and 1-butanol have also been explored [8].

Edible oils are the most important raw material for biodiesel production. The most commonly used oil is soybean oil with a share of 35%, followed by rapeseed oil 28% and palm oil (2011 data) [9]. Non-edible oils like Jatropha, Pongamia and neem are promising feedstocks in developing countries where edible oils are in short supply [10]. Today, Jatropha oil is already used for the production of biodiesel in India, where the annual production is estimated between 140 and 300 million liters per year [11].

However, ethical issues (food versus fuel discussion) have slowed down the introduction and use of first generation biofuels. For this reason, the use of lignocellulosic biomass (also known as woody biomass) has attracted considerable attention. Second generation biofuels potentially offer greater cost and CO_2 reduction

potential in the longer term. Possible lignocellulosic feeds include wood and agricultural residues like straw, grass, forest residues, bagasse, nuts and corn stover, and purpose-grown energy crops such as vegetative grasses and short rotation forests.

1.2. Global interest in *Jatropha curcas* L.

The last decade, *Jatropha curcas* L. (JCL) has received a lot of attention as its seeds contain an oil that is suitable for power generation or for the production of biodiesel. This development was initiated by a Wall Street Journal article in December 2007, highlighting an internal report from Goldman Sachs stating that JCL is one of the best candidates for future biodiesel production [12]. Arguments were the high seed oil content [13], the potential for high oil production levels per unit area in sub-humid tropical and subtropical climates [14], its drought-resistance and ability to grow well in marginal soils, though evidently this will have a negative effect on the oil productivity [15].

Typical seed production levels have been summarized by van Achten, *et. al*. [16] and are between 100-6700 kg seeds per ha per year. Climatic factors (e.g., temperature, precipitation, sunshine etc.), soil type, altitude and variety are known to have a significant effect on seed yield and oil content [17]. Akintayo (2004) reported that the seeds contain 47.3 ± 1.3% of crude oil, while the remainder being proteins (24.6 ± 1.4%), water (5.5 ± 0.2%), crude fiber (10.1 ± 0.5 %), ash (4.5 ± 0.1%) and carbohydrates (8% by difference) [18]. Achten reported an average oil content of the seeds of 34.4 wt% based on at least 10 different studies [16]. Unlike other major biofuel crops, JCL is not a food crop since the oil is non-edible due to the presence of toxins such as curcins, phorbol esters, trypsin inhibitors, lectins and phytates [19-21]. As such, it may be considered a second generation feed for biofuel production.

The Jatropha oil can be used as a biofuel directly in older diesel engines without any modifications [16,22], or processed further into biodiesel and aviation fuels [23]. Biodiesel from Jatropha oil is reported to give lower particulate matter emission [24]. In addition, the cetane number (51) of Jatropha biodiesel is higher compared to fossil diesel (46–50).

Besides for biodiesel production, numerous applications for JCL products have been mentioned in the literature, of which some are very old (Figure 2). Traditionally, JCL is used as a hedging plant and sheltering belt to protect agriculture and livestocks and as a fertilizer by providing humus to the soil [25]. The leaves of the plant are used to make tea to treat malaria and the sap is used to stop bleeding [26]. It is a herbal drug in Unani medicines and used against dental complaints. The milky sap of Jatropha is used in Mesoamerica for the treatment of different dermato-mucosal diseases [27].

Other plant parts like the woody residues and fruit parts can also be valorized. An example is the conversion of the press cake after oil extraction as animal feed and

ethanol/biogas production. The use of the fruit coats and seed hulls as fertilizer has also been reported because of their high concentration of nitrogen and other minerals [28].

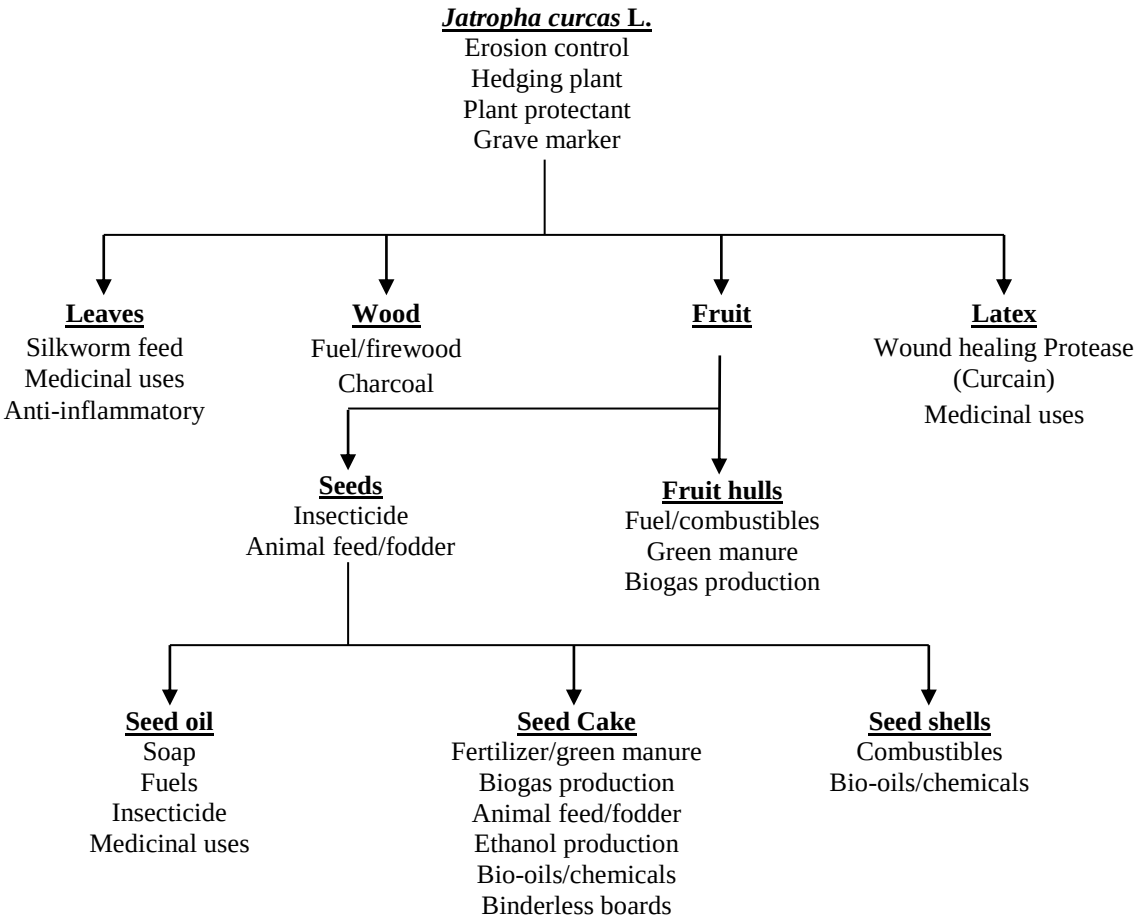

Figure 2. Possible applications of the *Jatropha curcas* L. plant (modified from [28])

Despite the potential for JCL cultivation, large scale plantations have to the best of our knowledge not materialized. A major issue is the oil productivity, which is lower than originally forecasted based on small scale trials under ideal conditions, and this seriously reduces the economic potential [12]. In addition, the JCL toxicity prevents the direct use of the seed cake for livestock feed, which otherwise would add significant value. The toxicity of the seeds and plant parts present a health risk to plantation workers, children and livestock. In addition, seed collection is labor intensive and mechanization is difficult to apply due to poor fruiting synchronicity. JCL seems more susceptible to pest and diseases when grown as a plantation mono-crop than originally anticipated. JCL may act as a host for certain cassava diseases and become a weed problem in certain environments [14].

1.3. Overview of energy resources and consumption in Indonesia

The large scale cultivation of renewable energy crops not only will have a major impact on global energy production systems, but is also regarded of high importance for

poverty reduction and rural development in many parts of the world [29]. Indonesia is a developing country with the highest population in Southeast Asia and the fourth most populous country in the world. Energy consumption in Indonesia has increased rapidly due to improved economics and population growth. According to the International Monetary Fund (IMF), Indonesia sustained relatively strong economic performance throughout the global recession, with an average GDP growth rate of just under 6% per annum for the past five years [30]. The Central Agency on Statistics of Indonesia (BPS) reported that total population in Indonesia rose from 205 million in 2000 to 239 million in 2012, and is projected to reach 273 million in 2025 [31].

To date, Indonesia is still heavily dependent on fossil resources for energy generation. Data from the Directorate General of Oil and Gas, Ministry of Energy and Mineral Resources shows that the total crude oil reserves (per January 1, 2011) in Indonesia is about 7.73 billion barrels. With an average production rate of 500 million barrels per year, the inventory would be exhausted in about 16 years. In the past decade, coal consumption has tripled and surpassed natural gas as the second most consumed fuel (2004 data).

The annual energy consumption increased from 778 million BOE (barrel of oil equivalent) in 2000 to 1.115 million BOE in 2011, which corresponds to an annual average increase of 3.9%. The energy consumption is mainly fossil based (83%), consisting of crude oil (41.5%), coal (23.4%) and natural gas (18.3%). The share of biomass (13.5%), hydropower (2.2%) and geothermal (1.2%) is limited [32].

In terms of annual CO_2 emissions, Indonesia emitted 406 million metric tons of CO_2 in 2008 and the volume increased slightly to 415 million metric tons in 2009. In 2011, Indonesia was the 15th largest CO_2 emitter in the world [33]. Emissions from the consumption of liquid petroleum products have been historically the primary source of fossil-related emissions and account for 36.6% of Indonesia's CO_2 emissions (2008). Emissions from coal usage increased sharply to 47 million metric tons of carbon surpassing emissions from liquid fuels for the first time in many years. Emissions from natural gas consumption, although quite variable, have risen steadily since the early 1970s and accounts for 15% of Indonesia's 2008 total emissions. With a population near 230 million people, Indonesia's emission is 0.49 metric tons of carbon per capita, which is well below the global average but has grown five-fold since the late 1960s [34].

1.4. Indonesia’s green energy policy

Indonesia is now a net importer of oil and economic growth is strongly affected by the global price of fossil fuels. Biofuels have increasingly attracted the attention of the Indonesian government because of their potential to reduce the dependence on fossil fuel and to meet global environmental requirements. The implementation of biofuels will reduce expenditure on fossil fuel subsidies.

Several regulations have been initiated by the Indonesian government to stimulate the development and use of alternative transportation fuels. Examples are the Presidential Regulation (Perpres 5/2006) on the National Energy Policy, the Presidential Instruction (Inpres 1/2006) on the utilization of biofuels and Presidential Decree No.10/2006 on the establishment of a national team for biofuels development. The National Energy Policy is intended to secure the national energy supply and to support sustainable national development. The Ministry of Energy and Mineral Resources (MEMR) has issued the National Energy Management Blueprint 2006-2025. The Blueprint (PEN) was prepared by the Secretariat of Energy Resources Technical Committee (PTE). It is a dynamic document that will be one of the leading national energy development references, covering the national strategy to manage and utilize the various energy resources including the roadmap for the alternative energy sector [35].

All initiatives are expected to have a major impact on the use of renewables for primary energy generation. The Energy Mix Target calls for a reduction in oil consumption by 20%, increasing coal use up to 33%, and increasing renewable energy to 17% by 2025, see Figure 3 for details.

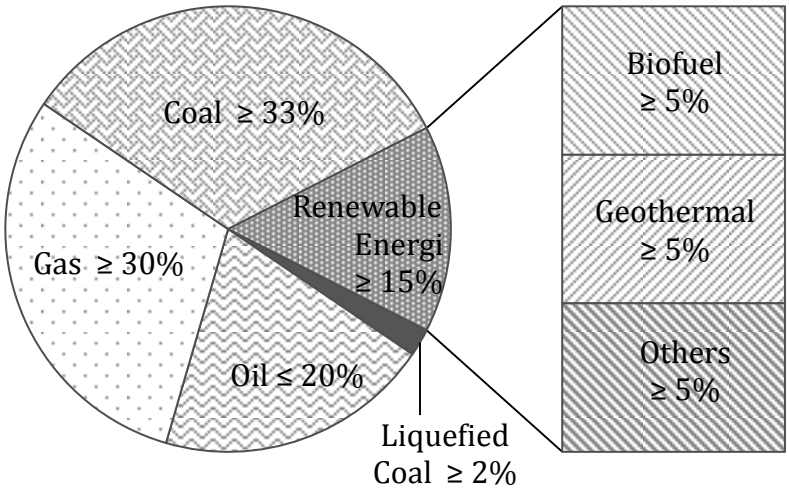

Figure 3. Targeted energy mix for Indonesia by 2025 [36]

To meet the renewable energy targets, biofuels play an important role. To reach the 5% target, 22.26 billion liters of biodiesel, bioethanol and bio-oil are required (Table 2).

Biodiesel has been identified as an attractive biofuel and its development has been actively stimulated by the Indonesian government. A plan for the introduction of biodiesel in Indonesia over a 25 years period has been prepared. The plan was launched in 2004 and execution is in progress since 2005. Three phases are considered. In the first phase (2005-2010), a minimum of 10% of automotive diesel oil (ADO), accounting

for 2% of the national energy consumption or equal to 2.41 million kilo liters, should be substituted by biodiesel from palm oil and other sources. The second phase (2011-2015) aims for a 15% biodiesel share and the introduction of other plant oils as raw material. In the third phase (2016 - 2025), the technology is expected to have reached the level of 'high performance' in which the products have excellent product properties like a high cetane number and low cloud point. The share of biodiesel is expected to meet 20% of ADO (5% of the national energy consumption) or equivalent to 10.22 million kilo liters.

Table 2. Roadmap for biofuel development in Indonesia

Biofuel type	2005–2010	2011–2015	2016–2025
Biodiesel	10% of diesel fuel consumption 2.41 mkL	15% of diesel fuel consumption 4.52 mkL	20% of diesel fuel consumption 10.22 mkL
Bioethanol	5% gasoline consumption 1.48 mkL	10% gasoline consumption 2.78 mkl	15% gasoline consumption 6.28 mkl
Bio-oil			
• Biokerosene	1 mkL	1.8 mkL	4.07 mkL
• Pure plant oil (PPO) for power plants	0.4 mkL	0.74 mkL	1.69 mkL
Biofuels	2% of energy mix	3% of energy mix	5% of energy mix
	5.29 mkL	9.84 mkL	22.26 mkL

mkL: million kiloliters

Actual biodiesel production in Indonesia has started in 2006 (65 million liters), increased 10-fold in 2008, but decreased to 330 million liters in 2009. The production showed strong growth again in the period 2010-2012, see Table 3 for details.

Table 3. Actual biodiesel data for Indonesia in 2006-2012 [37]

Calendar Year	2006	2007	2008	2009	2010	2011	2012
Production (Million Liters)	65	270	630	330	740	1,575	2,200
Exports (Million Liters)	33	257	610	204	563	1,225	1,500
Consumption (Million Liters)	5	22	23	60	220	358	670
Number of unit productions	2	7	14	20	22	22	26
Name plate Capacity (Million Liters)	215	1,709	3,138	3,528	3,936	3,936	4,280
Capacity Use (%)	30.2	15.8	20.1	9.4	18.8	40.0	51.4

Table 3 also shows the consumption of biodiesel in Indonesia in the period 2006-2012 [37]. Biodiesel consumption increased from 358 million liters in 2011 to 670 million liters in 2012 due to increased blending shares (5% in 2011 to 7.5% in 2012)

and the expansion of biodiesel distribution to East Kalimantan. However, domestic use is less important than export and more than 70% of the biodiesel produced in Indonesia is currently exported. The requirement of a blending rate of 10 percent in the fourth quarter of 2013 is expected to increase the Indonesian biodiesel consumption to reach 800 million liters. A further increase to 1 billion liters in 2014 can be achieved by expanding biodiesel distribution to Sulawesi Island and three other provinces in Kalimantan. A major constraint for Indonesian biodiesel producers is the high costs of inter-island shipping, which can add up to $60-120 per metric ton. The anti-dumping duties imposed by the European Commission may also lead to significant reductions of Indonesian biodiesel production in the future. Predictions indicate that the Indonesian biodiesel production in 2013 will be at the same level as 2012 (2200 million liters).

Recently, additional policies and programs have been launched by the Indonesian government to stimulate domestic biofuel consumption [38]:

- Indonesian gas retailers have the obligation to sell biofuels as per May 1st, 2012.
- Indonesian coal and mineral mining companies have to use 2% of biofuels in their total fuel consumption as per July 1, 2012.
- Indonesia's largest state-owned oil company, PERTAMINA has increased its blending rate from 5 to 7.5% as of February 15, 2012 and expanded distribution outlets of biodiesel in West Kalimantan province by August 2012.
- The Indonesian Ministry of Energy and Mineral Resources (MEMR) and Parliament reached an agreement to provide biofuel subsidies at 3.000 IDR per liter for biodiesel, and 3,500 IDR per liter for ethanol in 2013.
- In exchange for receiving subsidies, all biofuel companies will allow the Ministry of Finance to audit their financial statements.

On July 2013, MEMR has amended Regulation No. 32/2008 concerning the provision, utilization and trade system for biofuels. The amendment gives obligations for the mineral and coal mining industry as well as power producers regarding liquid biofuels. Administrative sanctions for producers not meeting the mandatory biofuel targets are also provided.

1.5. *Jatropha curcas* L. developments in Indonesia

In the last decade, JCL has strongly been promoted as a feedstock for biodiesel production in Indonesia. Since it is a non-edible oil, it does not directly compete with food products, though indirect competition with land and water supply is inevitably present. The three most mentioned feedstocks for biodiesel production in Indonesia are palm, JCL and coconut oil. Limited supplies of domestic coconut and Jatropha oil make them less competitive when compared to palm oil. Moreover, a relatively low oil yield per ha makes JCL-based biodiesel economically less viable [16]. Research activities to increase the economic value of JCL by breeding high yield varieties and increasing the value added of byproducts from the milling process such as JCL meal and glycerol are ongoing [37]. Table 4 shows the development plan for palm and JCL plantations as

released by the Ministry of Agriculture in 2006. The data are based on the biodiesel production targets.

Table 4. Plantation Development Plan 2007-2010 (in ha) [39]

No.	Plantation	2007	2008	2009	2010	Total
1	Palm oil	473.265	473.265	473.265	473.265	1.893.060
2	*Jatropha curcas* L.	341.000	345.000	360.000	375.000	1.461.000

According to the Indonesian government, an area of 94,000 ha was already cultivated with JCL nationwide by the end of December 2007 [40]. It is estimated that about 14.28 million ha is in principle very suitable for JCL plantations. Fig. 4 shows suitable areas for JCL plantations in Indonesia.

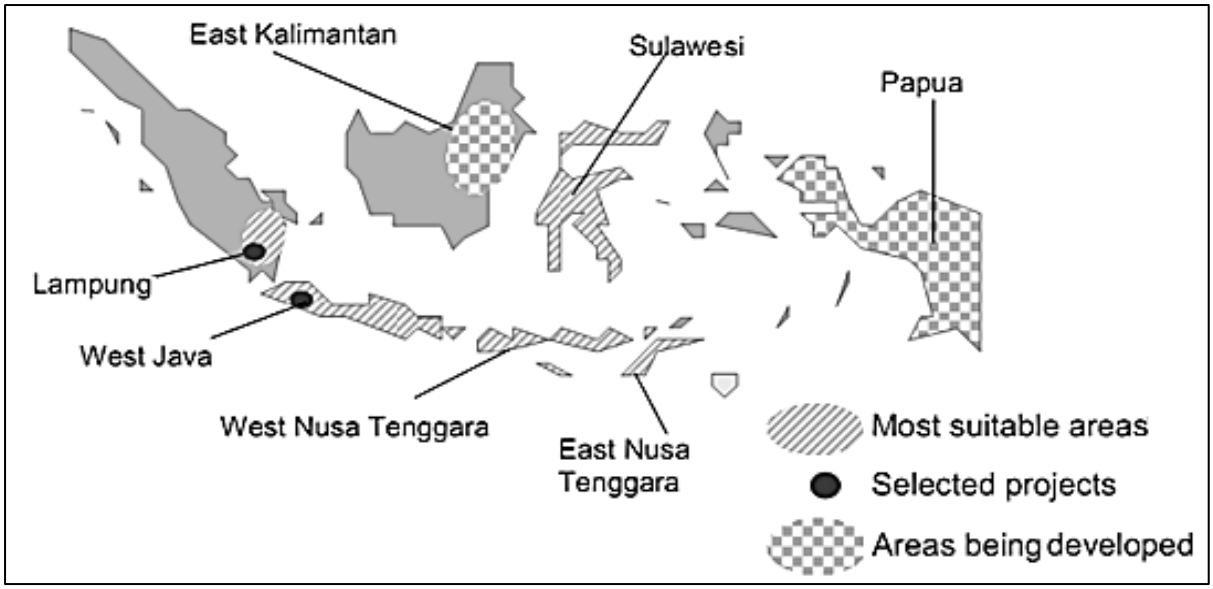

Figure 4. *Jatropha curcas* L. plantations in Indonesia (41)

At present, JCL plantations are found in West Nusa Tenggara, East Nusa Tenggara, West Java, Lampung and Sulawesi [41]. More plantations are reported to be developed in Nanggroe Aceh Darussalam, West and Middle of Java, South Sulawesi, and especially in the dry south eastern part of South Nusa Islands [40]. However, it is very hard to obtain accurate and reliable information and the actual status regarding JCL plantations in Indonesia is unclear at the moment.

Though JCL has a major role in the domestic biofuel policy, the number of commercial projects appears very limited. A combination of factors is likely the cause. Firstly, the various technologies in the value chain such as cultivation, variety selection, post-harvest and processing equipment are still in an early stages of research and development. For example, the productivity per hectare is still low and needs to be increased dramatically. Secondly, public awareness for the potential of JCL in large parts of the Indonesian society is absent. Thirdly, the development of an overall value chain

(plantation, harvesting, oil isolation, biodiesel production, markets) has received insufficient attention and is underdeveloped. According to local developers in Indonesia, a business model for JCL based biofuels is not feasible without taking into account revenues from byproducts [42]. A possible methodology to valorize the byproduct in an integrated manner is provided by the biorefinery concept.

1.6. The biorefinery concept

The International Energy Agency has defined biorefining as the sustainable processing of biomass into a spectrum of bio-based products (food, feed, chemicals, materials) and bioenergy (biofuels, power and/or heat) as illustrated in Fig. 5. NREL defines a biorefinery as a facility that integrates biomass conversion processes and equipment to produce fuels, power, and value-added chemicals from biomass [43]. The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum.

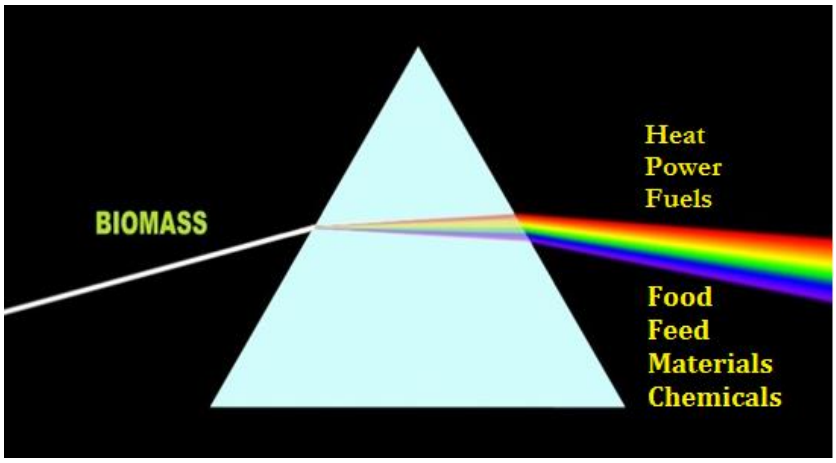

Figure 5. Biorefinery concept [44]

Biorefining aims at full valorization of the biomass source by performing the overall processes with a minimum loss of energy and mass, and by maximizing the overall value of the production chain [45,46]. It consists of efficient fractionations/conversions of the biomass source into various value-added products and energy using (physical) separation processes in combination with (bio)chemical and thermo-chemical conversion steps [46]. By producing multiple products, a biorefinery takes advantage of the various components in biomass and their intermediates therefore maximizing the value derived from the biomass feedstock. A biorefinery could, for example, produce one or several low-volume, but high-value, chemical or nutraceutical products and a low-value, but high-volume liquid transportation fuel such as biodiesel or bioethanol while at the same time generating electricity and process heat, through combined heat and power (CHP) technology, for its own use and on the marketplace. The high-value products increase profitability, the high-volume fuels are the cash cows, and the power production reduces energy costs and greenhouse gas emissions from traditional power plant facilities.

Large-scale biorefineries are already in operation. Examples are the production of soy oil and soy protein from soy, wheat starch and gluten from wheat and potato starch and protein from potatoes [47]. However, these existing biorefineries produce predominantly food products.

A possible biorefinery scheme for JCL is given in Fig. 6 and is explored in detail in the SPIN-2 project "Valorization of the JCL plant using the biorefinery concept". This project, funded by the Royal Dutch Academy of Sciences (KNAW) has, in contrast to conventional biorefineries, a strong focus on non-food applications.

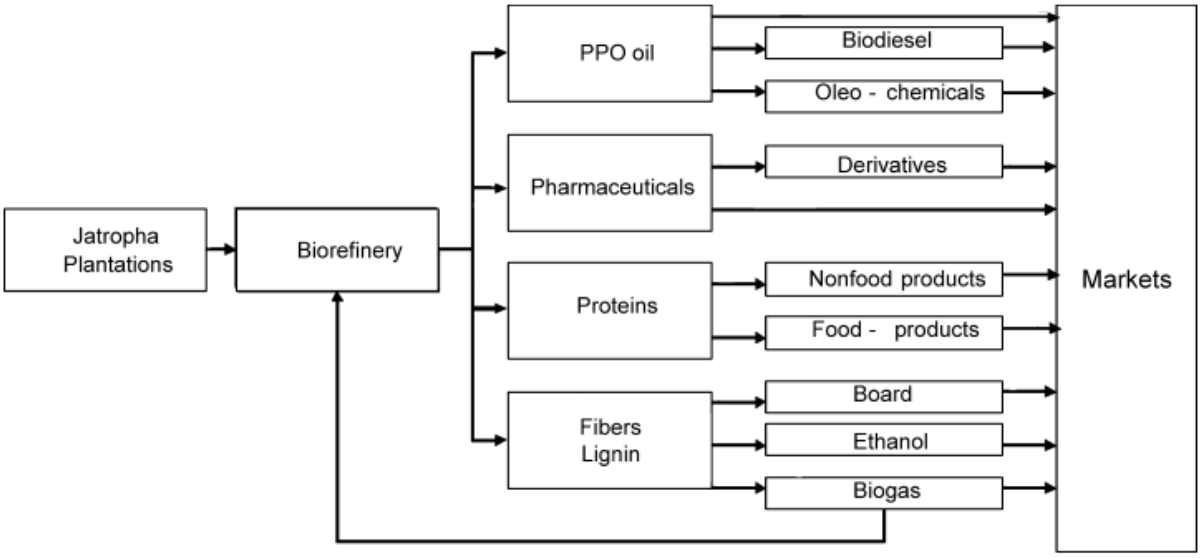

Figure 6. A simplified scheme for a JCL biorefinery [47]

1.7. Seed cake valorization

The term seed cake (press cake or oil cake) refers to the solids remaining after removal of the oil from plant seeds. Seed cakes are produced in the food/feed industry, examples are safflower seed cake (*Charthamustinctorius* L.) [48,49], sunflower seed cake (*Helianthusannuus*) [50], peanut press cake [51], soybean press cake [52], and coconut flesh [53]. Non-food seed cakes are obtained from the extraction process of flax seed (linseed) [54], rapeseed [55] and cotton seed [56]. Seed cakes may be toxic, for example cotton seed contains a toxic pigment, gossypol and JCL seed cake contains phorbol esters.

Seed cakes may be used for various applications. The simplest is the use as a green manure/fertilizer, animal feed (fodder) and as a fuel. In addition, technology has been developed to convert the cake into value added products such as bio-gas, bio-oils, activated carbon, fuel pellets and chemicals [57-59].

The conversion of the seed cake into value added products is possible by three main processes; biochemical, physico-chemical and thermo-chemical processes (Figure 7). Biochemical processes involve treatment of the press cake with micro-organisms at

temperatures typically below 80°C. Examples are fermentation and anaerobic digestion to convert the seed cake into ethanol and biogas, respectively. These processes are preferred for wastes having a high percentage of organic biodegradable matter and high moisture content. Anaerobic digestion generates gases with a high methane content (55–65 %) and a residue known as digestate which can be used as a soil conditioner. Ethanol fermentation involves the transformation of the organic fraction of the waste to ethanol by a series of biochemical reactions using specialized microorganisms [60].

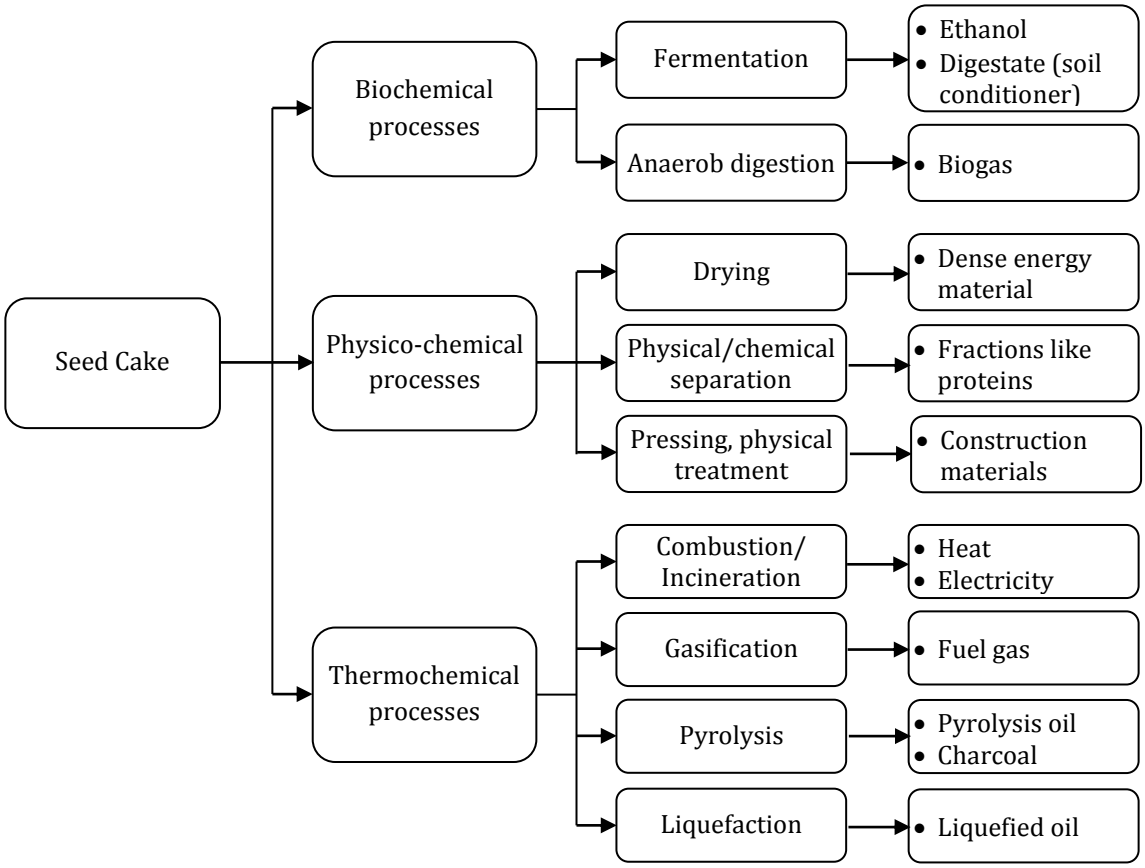

Figure 7. Seed cake conversion pathways

Physico-chemical processes involve seed cake conversions through physical separation and chemical reactions such as treatments with steam, water and other dedicated chemicals [61]. For example, the combustible fraction of the seed cake may be converted into fuel pellets which may be used for steam generation. This process involves drying of the seedcake, mechanical removal of sand, grit, and other incombustible matters and subsequent compacting and shaping into pellets [60]. Another process example is the recovery of proteins from JCL seed cake for non-food application by several physical and chemical treatments (59).

Thermochemical pathways offer opportunities for the rapid and efficient processing of the seed cake into fuels, chemicals and energy. Thermochemical processing has several advantages compared to biochemical processing, including

greater feedstock flexibility, conversion of both the carbohydrate and lignin fraction into valuable products, faster reaction rates, and the ability to produce a wide range of different biofuels [62]. An example of a thermochemical process is pyrolysis, which is in essence the thermal decomposition of the cake in an inert atmosphere at about 400-600°C [63]. Other examples of thermochemical processes are combustion, gasification and liquefaction [64].

1.8. Thesis outline

This thesis describes the results of experimental studies on the valorization of JCL seed cake. The primary objective of the research described in this thesis was to identify sustainable routes for the conversion of JCL seed cake into higher added-value products for non-food applications. Only physico-chemical and thermochemical processes were explored, while biochemical ones were not taken into account.

In **Chapter 2,** experimental studies on the use of the JCL seed cake as a raw material for binderless boards are described. It involves treatment of the cake at elevated temperature and pressures to induce chemical reactions to increase the mechanical strength of the material and thus allow its use as a board, for instance, in the construction industry. The effects of the cake water content (5–20 wt%), pressing conditions such as pressing temperature (120–200˚C), pressure (50–150 bar), and heating time (30-60 min), on the physico–mechanical properties of the resulting binderless boards were determined using an experimental design approach. The mechanical properties of the resulting binderless board were compared with typical commercial particle boards. The effect of the addition of hemp woody core particles on the board properties was evaluated.

Chapter 3 presents a study on the liquefaction of JCL seed cake in four different solvent in the presence of hydrogen, either with or without the use of a catalyst (Na_2CO_3, Fe-limonite). The experiments were carried out in a batch autoclave at a temperature of 300°C, 5 MPa of initial hydrogen pressure and 30 min reaction time. Seed cake conversion, oil yields, and relevant chemical properties of the product oils were investigated.

Chapter 4 deals with the conversion of the JCL seed cake by fast pyrolysis. Products yield - process condition relations were established. Relevant properties of the bio-oils obtained at a fixed pyrolysis temperature (507°C) were determined.

Chapter 5 deals with the conversion of JCL seed shells (nut shell) to pyrolysis oil by a fast pyrolysis process. The experiments were carried out in a continuous bench scale rotating cone fast pyrolyzer with a throughput of 2.27 kg/h at 480°C and atmospheric pressure. Relevant properties of the oil were determined.

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Chapter 2

Preparation and Properties of Binderless Boards from *Jatropha curcas* L. Seed Cake

H. Hidayat, E.R.P. Keijsers, U. Prijanto, J.E.G. van Dam, and H.J. Heeres

Abstract

The potential of *Jatropha curcas* L. seed cake after oil extraction (expelling of seeds followed by hexane extraction) as a raw material for binderless boards was investigated. The composition of the de-oiled seed cake was investigated using a range of techniques (proximate-, ultimate analysis, TG/DG, SEM). The effects of pressing conditions like the water content of the feed material (5–20 wt%), pressing temperature (120–200°C), pressure (5–15 MPa), and heating time (30-60 min) on the physico–mechanical properties of the resulting fiber boards were determined. The optimum conditions were 8 wt% moisture content, a pressing temperature at 135°C, 10 MPa pressure, and heating and cooling times of 30 and 15 min, respectively. The mechanical properties of the binderless boards are comparable with typical commercial particle boards. The effect of the addition of hemp woody core particles on the board properties was evaluated and small but clear synergistic effects were observed.

2.1. Introduction

Jatropha curcas L. (JCL), also known as physic nut, is a multipurpose tropical plant that can be used to reclaim and improve the quality of dry and degraded land [1,2]. Recently, JCL has received a great deal of attention because it produces a non-food oil that is very suitable for biodiesel production. JCL seeds contain around 47.3 ± 1.3% of crude oil, the remainder being proteins (24.6 ± 1.4%), water (5.5 ± 0.2%), crude fibers (10.1 ± 0.5 %), ash (4.5 ± 0.1%) and carbohydrates (8% by difference) [3].

Several oil extraction methods for JCL seeds have been investigated. The use of mechanical extraction with expellers is the most popular because it is a simple, continuous, flexible and safe technology, although relatively low oil yields are obtained [4]. Mechanical extraction is performed using the whole seeds (shells and kernels), partly dehulled or solely the kernels as feed. Typical oil extraction yields for screw presses are between 90-95%. The residue after oil extraction is known as the seed- or press cake. Staubmann*, et. al.* (1997) reported that the seed cake contains crude proteins (27%), lipids (7%), and fibers (35.5%, calculated on dry basis)[5]. The residual amount of oil in the seed cake depends on the extraction technology, processing conditions and the feed (whole seeds or kernel only). In case of mechanical extraction of whole seeds, the oil content of the seed cake is much higher than when using kernels only [6].

There is a clear incentive to valorize the seed cake after oil extraction. Various outlets have been identified for seed cakes from various plant seeds. Examples are the use as animal feed, for biogas production and as a fertilizer. JCL seed cake is not directly suitable as an animal feed because of the presence of toxic compounds such as curcins and phorbolic esters [7,8]. The utilization of the JCL seed cake to produce biogas with a high content of methane by means of anaerobic fermentation and gasification has been investigated [5,9]. The JCL seed cake as well as other by-products of JCL, such as the fruit coats and seed hulls can also be used as organic fertilizers [10-12].

We report here the use of JCL seed cake obtained from expelling JCL seeds followed by hexane extraction as a raw material for binderless board manufacture with opportunities to be used as construction materials. Binderless boards do not require the use of external adhesives and utilize the intrinsic adhesive capacity of the various biopolymers present in the feeds. As such, the use of expensive, non-renewable synthetic resins is avoided. The use of lignocellulosic wastes for binderless board manufacture has been explored recently and examples are coconut husks [13], bagasse [14], banana bunch [15], and oil palm trunk [16]. Parameters that affect board properties have been identified and include processing parameters such as pressure, temperature, time of pressing and properties of the feed materials such as type, size and shape of the particles and moisture content. Some additional physical and chemical treatments have been proposed to improve the quality of the boards [17-20]. This chapter describes an experimental study on the use of JCL seed cake (including seed shells) as raw material for binderless board production. Experimental boards were

produced using a conventional hot pressing method. The effect of process variables on relevant physico-chemical properties of the boards has been established and will be reported.

2.2. Experimental

2.2.1. Materials

JCL seeds were obtained from ITB Bandung Indonesia and originated from a plantation in Subang. JCL seed cake was produced at room temperature using an expeller processing unit at B2TE – BPPT Indonesia. The seeds including the shells were processed. The JCL seeds and seed cake were stored at 4°C to inhibit thermal and microbiological degradation. The seed cake was crushed to particle sizes less than 1 mm using a hammer mill. Residual oil in the crushed seed cake was removed using a hexane extraction in a continuous extraction unit (Pilot Pflanzenöltechnologie Magdeburg e.V.) at a scale of 70 kg. The de-oiled seed cake (DOSC) was used as the raw material for the binderless board.

2.2.2. Composition of relevant JCL samples

The average moisture, oil, protein and ash content of the JCL samples (seed shell, seed kernel and seed cake) were determined using established procedures. The moisture content of the samples was determined by weighing the samples before and after drying at 103°C for 24 h. Protein analyses were performed using Kjeldahl method [21] and a factor of 6.25 was applied for the conversion of nitrogen content to protein values [22]. The oil content of the samples was determined using a soxtec method (Avanti 2050 Auto System) using hexane as the solvent [23]. Ash content was determined gravimetrically. The sample was weighted, placed in an oven at 575°C for 180 min and again weighted. The residue was taken as the ash content.

2.2.3. Chemical composition of de-oiled samples

The de-oiled samples were milled and sieved (0.5 mm) before analysis (extractives, polysaccharide composition, uronic acids and lignin content). The samples were extracted using a soxtec method (Avanti 2050 Auto System) with ethanol/toluene 2/1 (v/v), followed by ethanol (96%), and, when required, with water for 1 h. The residues were dried at 40°C for 16 h, and subsequently analyzed. The neutral sugars and lignin content were determined after a two-step hydrolysis of the ethanol-extracted material using sulfuric acid (12 M) at 30°C for 1 h followed by a treatment with sulfuric acid (1 M) at 100°C for 3 h according to modified TAPPI methods [24-26]. Neutral sugars were determined by HPAEC with pulsed amperometric detection on a CarboPac PA1 column (Dionex) with a water-sodium hydroxide gradient [27]. The acid insoluble lignin in the hydrolysate was measured by weight as Klason lignin, whereas the soluble

lignin content was determined by a spectrophotometric determination at 205 nm [28]. Uronic acids in the sulfuric acid hydrolysate were spectrophotometrically determined at a wave length of 520 nm [29]. All samples were analyzed in duplo and the average value is reported.

2.2.4. Experimental procedure to isolate individual fraction of the samples

The separation of crude fibers from the JCL seed cake, seed shells and seed kernels were performed by a sequence of extraction steps [30], see Fig. 1 for details. The sample was crushed to particle sizes less than 0.5 mm, and then extracted using a soxhlet method with hexane (95%, Sigma) to remove the residual oil. A solid to liquid ratio of 1/10 (w/v) was used and 10 h extraction time was applied. The de-oiled sample was stirred for 3 h in a basic solution (NaOH 0.055M, 85%, Merck) at room temperature with a solid to liquid ratio of 1/10 (w/v) to remove the proteins [31]. The liquid was separated from the solids by centrifugation using a Sorvall centrifuge at 4000g for 15 min, and then the remaining NaOH in the solid was removed using a wash step with distilled water. This procedure was repeated until the pH of the solution was neutral. The deproteined sample was treated with an α-amylase solution (Sigma, 10 vol% enzyme in solution) with a liquid to solid ratio of 10/10 (v/v), and stirred at 60-70°C for 1 h to solubilize the starch. The sample was subsequently washed with ethanol/toluene 2/1 (v/v) at a liquid to solid ratio of 10/1 (v/v) for 1 h and subsequently with boiling water for 1 h. The resulting final sample was dried for 24 h at 80°C. The ash content was determined by placing the sample in an oven at 575°C for 180 min. The crude fiber content is defined as the weight of the final sample (excluding ash) divided by the initial weight of the JCL sample.

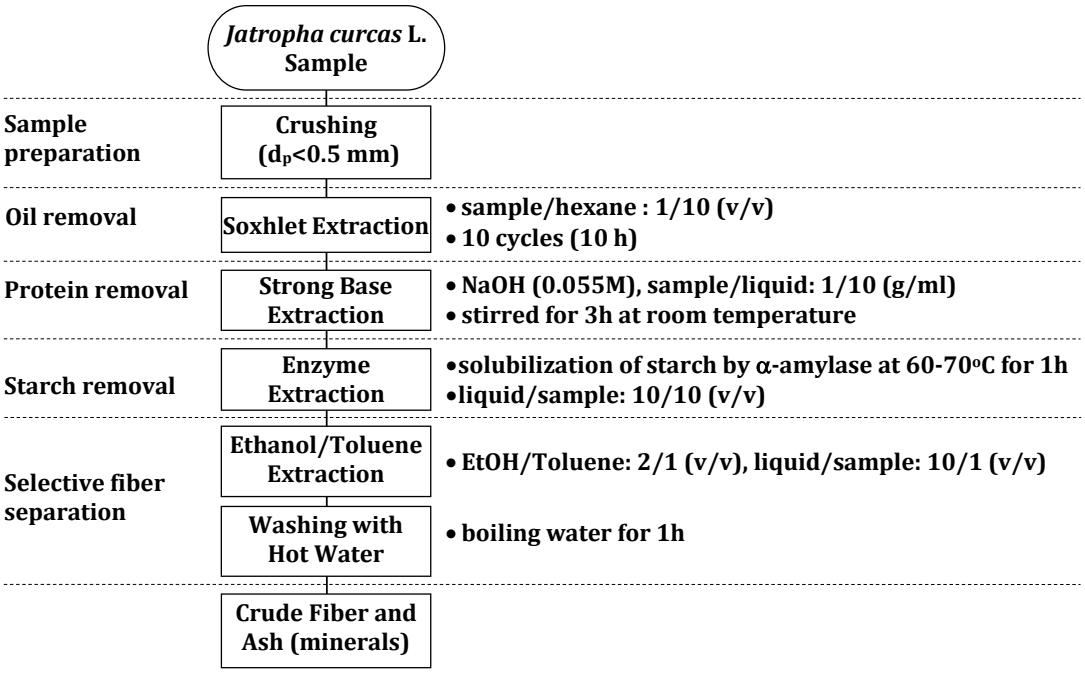

Figure 1. Experimental procedure for crude fiber isolation

2.2.5. SEM (Scanning Electron Microscope) analysis

A JEOL JSM-6500F SEM operated at an accelerating voltage of 20 kV was used to determine the surface morphology of the samples. Before analysis, the samples were cooled in liquid nitrogen and crushed with a plier. The samples were coated with platinum using a sputter coater (Oxford CTI 1500). The SEM images were taken at the fractured surfaces of the sample.

2.2.6. Differential Scanning Calorimetry (DSC)

DSC spectra were recorded on a Perkin-Elmer DSC-7 equipped with Pyris software. The DSC was calibrated with Gallium and Indium. Deflection of the instrument was corrected by substraction of the corrected empty pan data from the sample data when run under exactly the same conditions. The upper temperature limit was set at 200°C. The samples (about 5 mg each) were weighed into a standard aluminum pan with a lid. Each sample was subjected to two measurements. For the first run, thermograms were recorded at a heating rate of 10°C/min between 0 to 200°C. For the second run, the sample at the end of the first run was cooled down to 0°C at an approximate rate of 6°C/min and the thermograms were recorded again at a heating rate of 10°C/min between 0 to 200°C.

2.2.7. Thermal Gravimetric Analysis (TGA)-measurements

A Perkin Elmer-TGA 7 equipped with Pyris software was used to determine the thermal behavior of the sample. Approximately 20 mg of sample was used and spectra were recorded between 30-900°C, at a 10°C/min heating rate. Oxygen was used as the purge gas at a flow rate of 20 ml/min.

2.2.8. Binderless board experiments

2.2.8.1. Board preparation

Binderless boards from de-oiled seed cake (DOSC) samples were prepared using a conventional laboratory hot press, see Fig. 2 for details.

The moisture content (MC) of starting materials was varied between 5-20%. The moisture content was determined using a drying step with a UV lamp. The sample was compressed using two circular mould halves. Open moulds were used, allowing the water vapor to escape during heating up. The DOSC sample was homogeneously distributed in the mould. Fiber boards of 30 cm diameter and with a target thickness of 6 mm were prepared. Hot pressing was performed at 120-200°C, a pressure between 5-15 MPa and holding times between 30 and 60 min. After hot pressing, the boards were cooled just below 100°C in the press while maintaining the pressure (about 15 min). Subsequently, the boards were conditioned under load by placing a metal plate

(thickness ± 5 cm and diameter ± 30 cm) on the boards in a conditioning chamber at a temperature of 20±3°C and a relative humidity of 50±1%.

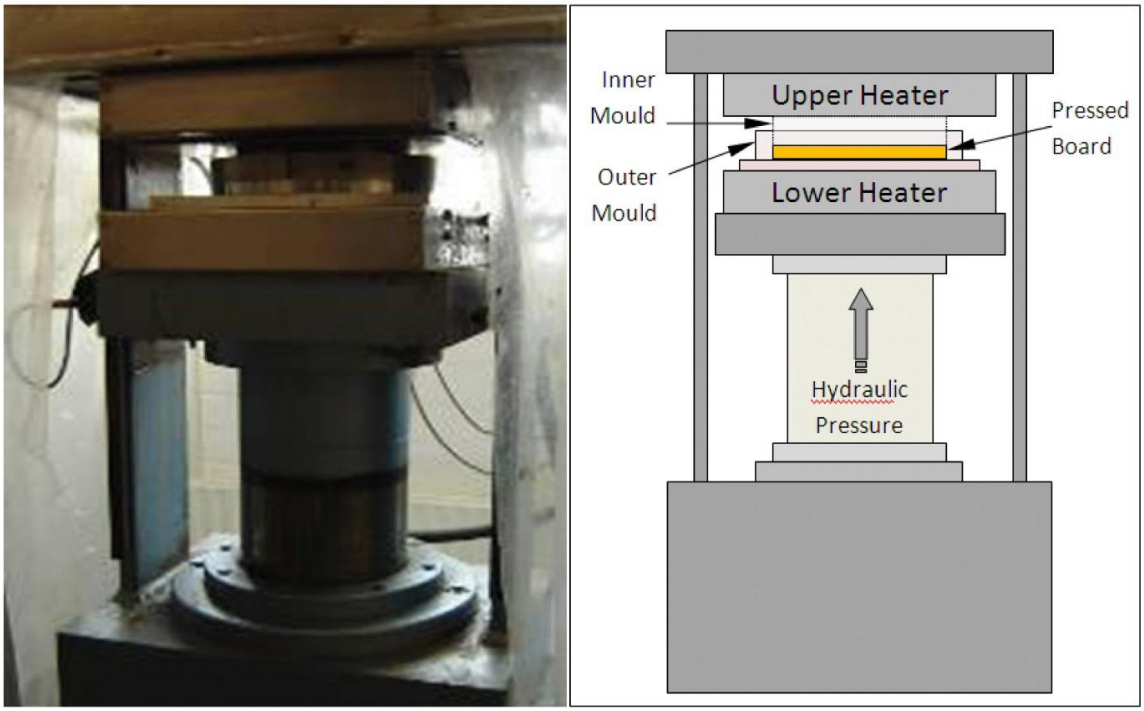

Figure 2. Picture and schematic representation of the hot press used in this investigation

2.2.8.2. Mechanical properties

The mechanical properties of the boards are expected to be a function of the moisture content of the samples. Therefore, the test samples were conditioned to constant moisture content in a conditioning chamber (relative humidity of 50±1% and a temperature of 20±3°C) for at least 1 week. Subsequently, the test specimens of 15 x 150 mm^2 were cut from the boards. The test specimen were subjected to flexural loading at a span length of 24 times the sample thickness. The flexural properties of the boards were evaluated in accordance with an ASTM procedure (D1037-99) on a Zwick 1445 [32]. The flexural strength and modulus were determined for 3 test bars per sample and the average value is reported.

2.2.8.3. Water absorption and thickness swelling

Water absorption and thickness swelling of the boards were evaluated by ASTM methods (D 1037-99 method B of section 105, single continuous 24 h submersion period) [32]. The dimensions and weight of the test specimens (ca. 15 x 50 mm^2) were determined accurately using a vernier caliper and an analytical balance, respectively. Subsequently the samples were immersed in demineralized water for 24 h at room temperature, and the dimensions and weight were determined again. From the

dimensions and weight data, the water absoption (wt%) and the thickness swelling (%) were determined. The analysis were performed in triplo per sample and the average value is reported.

2.2.8.4. Data analysis on binderless board properties

The experimental results for each response (modulus and strength) were analyzed statistically by means of the Design Expert 8 software package (Stat-Ease Inc.). The responses (y_k) were modeled with a quadratic model using the following standard expression:

$$y_k = b_0 + \sum_{i=1}^{4} b_i x_i + \sum_{i=1}^{4} b_{ii} x_i^2 + \sum_{\substack{i=1 \\ i \neq j}}^{4} \sum_{j=2}^{4} b_{ij} x_i x_j \quad (1)$$

Here, i represents the independent variables T, P, t (holding time) and moisture content (MC) while b_i, b_{ii}, b_{ij} are the regression coefficients which were obtained by statistical analysis of the data. The significant factors were selected based on their *p*-value in the analysis of variance (ANOVA). Factors with a *p*-value below 0.05 were regarded as significant and included in the response model. Step-wise elimination was applied to eliminate all statistically insignificant terms. After each elimination step, a new ANOVA table was generated until all insignificant factors were removed.

2.3. Results and discussion

2.3.1. Morphological characteristics of JCL seeds

The JCL seed consists of a hard black nut shell and a soft white kernel containing the plant oil in a protein rich matrix [33]. Analysis shows that the JCL seeds used in this study consist on average of 61.6 wt% (dry basis) of kernel and 38.4% of shell. These values are within the ranges reported by Makkar, *et. al*. (1998); *viz* 60.0 - 63.5% for the kernel and 36.5 - 40.0% for the shell [34].

SEM micrographs of the cross surface of the shell show that it consists of two layers (Fig. 3A). The outer layer is black and very hard. The inner shell is composed of uniform parallel duct shaped layers oriented perpendicular to the hard outer surface. These layers are softer than the outer skin layer. A cross section view of the inner shell (Fig. 3B) shows clusters of hollow circular ducts with a diameter of about 10 μm. The fibers in the shell, hairy-like materials that form continuous filaments, are located in the hollow circular ducts and have a diameter of around 1.2 μm (Fig. 3C) and a length of about 300 μm which is similar to the thickness of the inner shell (Fig. 3A). SEM micrographs of the kernels do not show any fiber-like structures, neither in cross nor parallel sections (Fig. 3 D-E). The kernel is characterized by a cellular structure with thin walls and intercellular spaces.

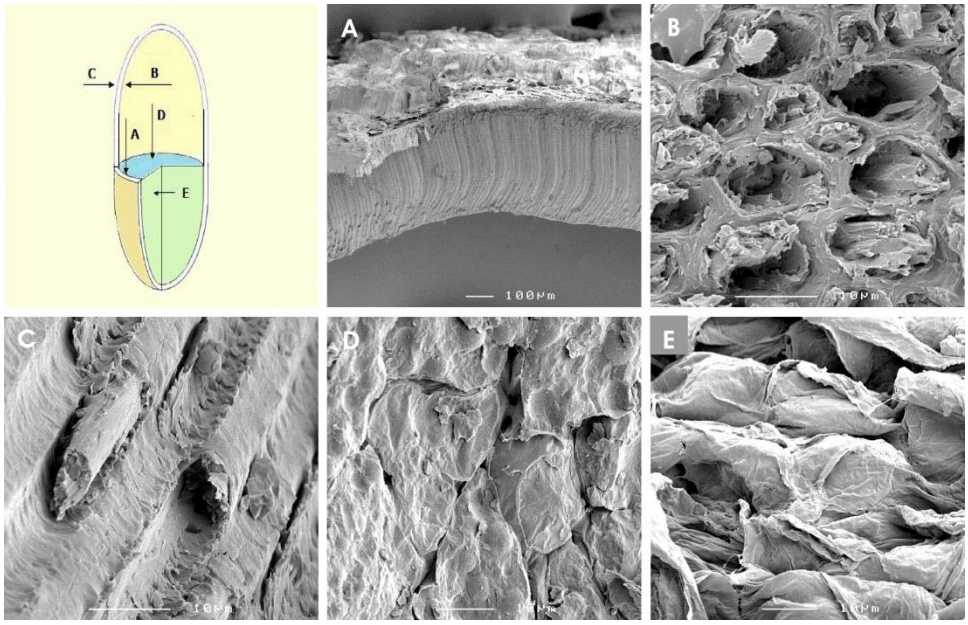

Figure 3. SEM pictures of JCL seed parts: (A) seed shell, cross view; (B) seed shell, inner layer; (C) seed shell, fibers in hollow ducts; (D) kernel, cross view; (E) kernel, parallel view

2.3.2. Chemical composition of JCL samples

The moisture, oil, protein, ash and crude fiber content of the JCL shells, kernels and seed cake after expelling were determined and the results are given in Table 1. The crude fiber content is the highest in the shells (63.8 wt%). The kernel and seed cake are rich in proteins (26.1 wt% and 28.4 wt%), in contrast to the shells which contain only 5.7 wt% proteins. The ash contents are below 6.2 wt% in all samples. As expected, the oil is mostly located in the kernel (51.6 wt%). The seed cake after oil extraction using a screw expeller still contains12.0 wt% of oil.

Table 1. Proximate analysis of original JCL samples[a]

Component	Seed Shell	Seed Kernel	Seed Cake[d]
Moisture	11.1	5.4	4.1
Oil (db)[b]	1.7	51.6	12.0
Protein (db)	5.7	26.1	28.4
Ash (db)	4.9	4.6	6.1
Crude fiber (db)	63.8	5.2	25.9
Others (db)[c]	23.9	12.5	27.6

[a] wt%; [b] db : dry basis; [c] by difference, others are lignin, hemicellulose and extractives; [d] after expelling

The amounts of extractives, sugars, uronic acid and lignin in de-oiled seed cake (DOSC), seed shell (DOSS) and seed kernel (DOSK) were also determined and the results are given in Table 2.

The content of hot water soluble components like easily soluble sugars, salts and smaller organic compounds (e.g. acids, aldehydes, aminoacids) in DOSS, DOSK, and DOSC are 5.29, 7.07 and 9.24% respectively. A clear difference in the total polysaccharide amount and composition between the samples is observed. The total polysaccharide content of the DOSS (44.21%) is substantially higher than of the DOSK (20.33%). In all samples, D-glucose is the major carbohydrate building block. In DOSS, the main glucose source is likely cellulose in the form of fibers, which are the major strucural component in the JCL seed shell (Table 1) [35]. In the DOSK, the glucose may also be derived from other glucans like starch. Next to glucose, xylose is present in DOSS in considerable amounts (12.11%). In woody tissues, xylan is the most common non-cellulosic polysaccharide and present in the hemicellulose fraction. Xylans often contain uronic acid branches and may occur in the form of glucuronoxylan, or xyloglucans, which are known to play key roles as structural plant cell wall components [36].

Table 2. Chemical composition of de-oiled JCL samples (wt% on dry basis)

Component	De-oiled seed shell (DOSS)	De-oiled seed kernel (DOSK)	De-oiled seed cake (DOSC)
Extractives (%)			
• Ethanol/ toluene	2.72	6.28	4.34
• Ethanol	0.54	2.49	1.36
• Hot water	5.29	7.07	9.24
Total Polysaccharides (%)	44.21	20.33	33.4
• Arabinose	0.66	2.42	1.27
• Xylose	12.11	1.16	7.34
• Mannose	1.30	0.34	0.96
• Galactose	0.97	1.61	1.01
• Glucose	28.85	14.62	22.60
• Rhamnose	0.31	0.18	0.23
Uronic Acids (%)	0.76	0.62	0.68
Total Lignin (%)	44.04	10.73	28.84
• acid insoluble lignin	43.71	9.80	28.25
• acid soluble lignin	0.33	0.92	0.59

The lignin content is highest for the DOSS, indicating that the shell is highly lignified. The lignins are mainly acid insoluble. The total lignin content for the DOSC (28.84%) is somewhat higher than the value of 23.91% reported by Sricharoenchaikul, *et. al.* (2007) [35]. The difference could be caused by many factors such as differences in JCL plant varieties, extraction process, or ascribed to differences in analytical methods.

Thus, it can be concluded that the DOSC, the main starting material in this chapter for the preparation of binderless boards, contains significant amounts of proteins, fibers and lignin. Some of these components (lignin, proteins and

carbohydrates) may serve as natural binders that can be activated and moulded (softened) under high pressures in the presence of moisture and cured at elevated temperature. The binding capacity of the natural glues is based upon a number of reactions and interactions: i) auto-cross-linking reactions of lignin, ii) hydrogen bonding between the polar carbohydrate components (cellulose, starch) and the lignin or proteins and iii) protein denaturation [37]. In addition, extractives often contain low molecular weight phenolics that may also contribute to the binding [38]. Based upon the chemical composition of DOSC (about 33.4% structural carbohydrates (cellulose and hemicellulose) and 28.8% lignin), different mechanisms of internal bonding can be expected.

2.3.3. Thermal properties by Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on three de-oiled samples: DOSS, DOSK and DOSC. All samples showed the occurrence of an endothermal process at low temperature (40-90°C, Fig. 4) and, depending on the sample, other exothermal and endothermal events between 120 and 180°C. For DOSC, two peaks appeared in the first heating cycle: an endothermic peak with a maximum at 64°C, and an exothermic peak at 145°C (Fig.4A). In a second heating cycle, the peaks were absent, indicative for the occurrence of irreversible reactions in the first heating cycle. Possible reactions are irreversible condensation (dehydration and cross-linking) reaction or curing of lignin-like components in the material [39]. A similar result was obtained for DOSS where an endothermic reaction is observed at 68°C, and an exothermic reaction at 152°C (Fig. 4B). A DSC analysis for DOSK showed four peaks, an endotherm at 53°C, an exotherm at 156°C, an endotherm at 167°C and an exotherm at 173°C (Fig. 4C). All peaks are absent in a second heating cycle. The thermal behavior indicates the occurrence of chemical (cross-) linking reactions between 40 and 185°C and these features are of importance when aiming for the production of binderless boards without using additional adhesives [13].

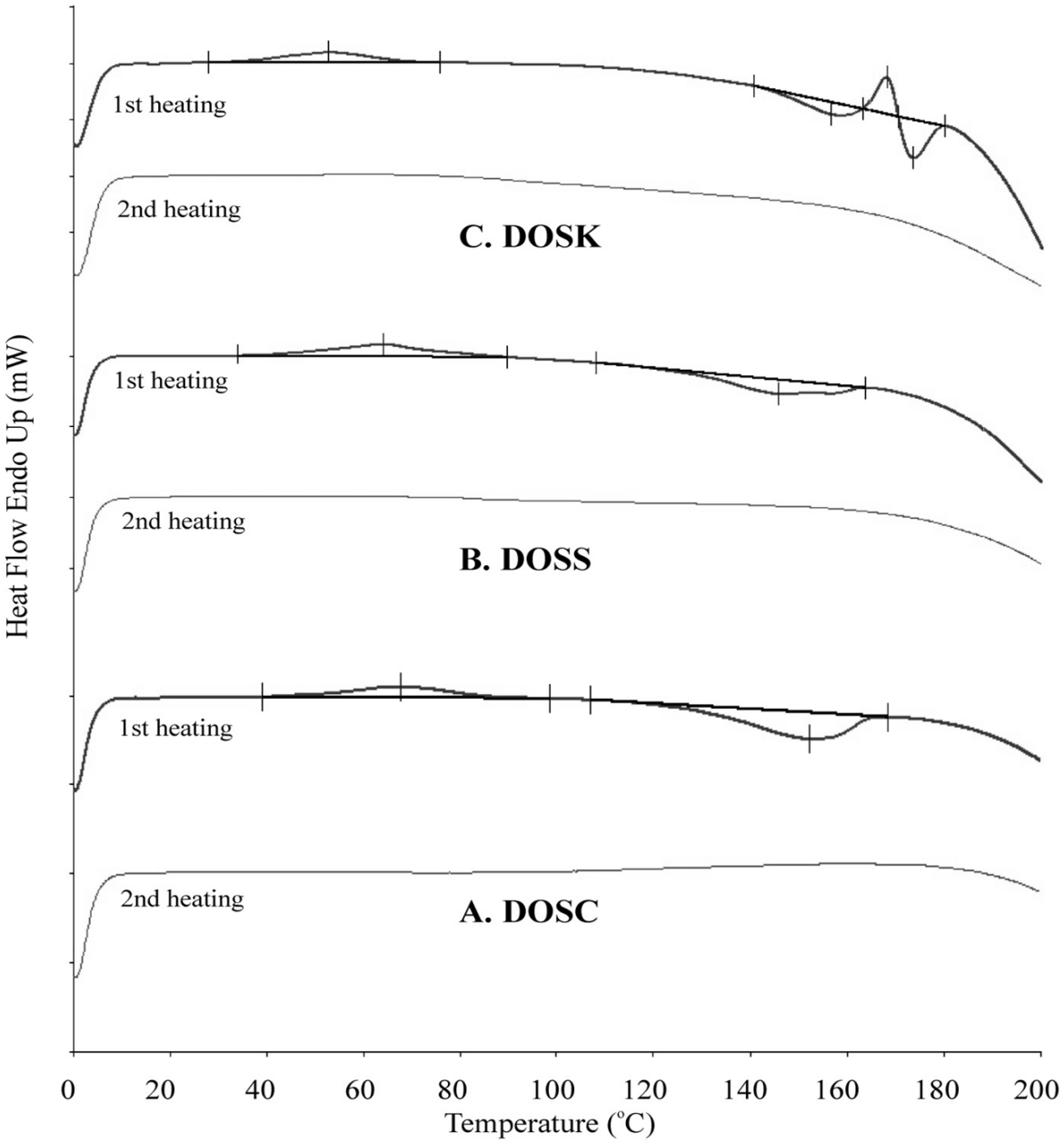

Figure 4. DSC spectra for de-oiled seed cake, de-oiled seed shell and de-oiled seed kernel

2.3.4. Thermal properties by Thermal Gravivetric/Differential Thermal Analysis (TG/DTA)

The thermal behavior of the seed cake is of relevance to determine the process condition for binderless board production. The thermal degradation behavior of the different JCL seed cake samples are shown in Fig. 5. Relevant TG/DTA data for the samples are given in Table 3. The samples include de-oiled seed cake and various fractions thereof obtained by the experimental procedure described in Figure 1. In addition, the results for the protein fraction of the seed cake, isolated by a published procedure [31], are provided. In general, the TG data for the JCL seed cake samples

show three major weight loss steps. The first with a maximum below 120°C for all samples is due to water evaporation. The second and the third weight loss peak were at about 320°C and in the range of 380-630°C, respectively.

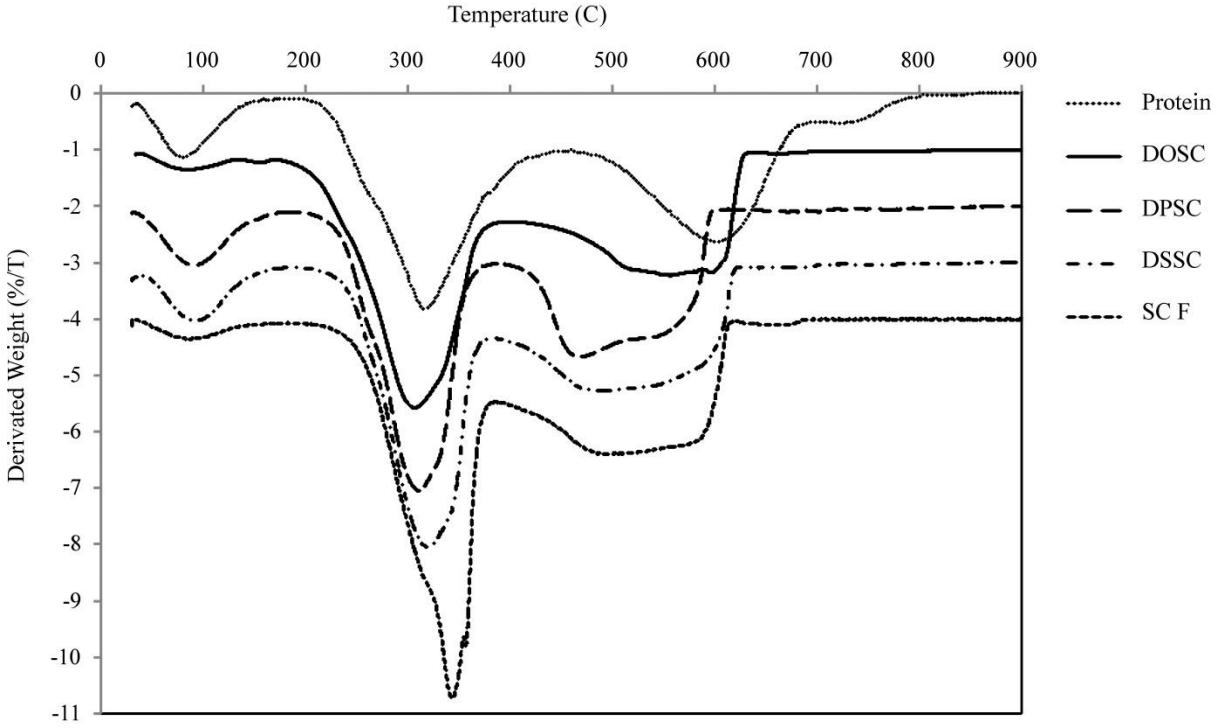

Figure 5. DT analysis of JCL seed cake after processing (DOSC: de-oiled seed cake; DPSC, deproteined seed cake; DSSC: de-starched seed cake; SCF: seed cake fiber; protein: JCL seed cake proteins)

Table 3. TG/DTA data for the various samples[a]

Sample	Onset temp for peak II (°C)	Peak Temperature (°C)			Moist. Cont. (%)	Weight loss (%)			Ash (%)
		II	III	IV		II	III	IV	
De-oiled seed cake	253	302	553	594	3.2	49.0	33.7	6.3	7.1
Deproteined seed cake	263	305	463	-	7.9	43.6	40.8	-	5.9
Destarched seed cake	272	314	483	-	7.4	43.2	44.0	-	3.9
Seed cake fiber	296	342	499	-	2.7	48.9	45.3	-	3.3
Proteins	262	313	-	600	7.8	46.9	-	40	3.5

[a]Peak I (<120°C) is associated with water removal and was obtained from the weight loss associated with peak I

DOSC starts to decompose at the lowest temperature (253°C onset temperature) followed by deproteinated seed cake, destarched seed cake, and seed cake fiber. The maximum weight loss of seed cake fiber occured at around 200-380°C with a peak temperature at 342°C (Table 3). The maximum weight loss of seed cake fiber is due to degradation of the hemicellulose and cellulose fraction in the fibers [35]. A second peak for seed cake fiber was observed between 380 and 620°C (Fig. 5) with a peak temperature of 499°C (Table 3). This broad peak likely is the result of lignin degradation, which is known to lead to broad peaks [40].

2.3.5. Binderless board preparation and properties

The seed cake after oil extraction of seeds using a screw expeller still contained 12.0% of oil and this remaining oil may have negative effects on the quality of the boards produced thereof. This was confirmed by initial screening experiments on binderless board preparation using oil containing seed cake. The resulting black colored boards were characterized by a strong, unpleasant odor. In addition, operational problems were encountered and the particles were ejected from the mould when subjected to high pressure and elevated temperature. Therefore the seed cake, shells and kernels were de-oiled before binderless board preparation using a hexane extraction.

The properties of the binderless board materials were evaluated in detail and include flexural strength, modulus and swelling indexes. Moreover, the use of hemp chips as a filler material was studied and a comparison was made with commercial boards. In addition, the microscopic structure of the boards was studied by SEM micrography, thermal behavior by TG/DTA analysis and change of surface chemistry of board particles by FTIR.

2.3.6. (Visual) appearance of the particle board samples

Figure 6 shows representative pictures of a binderless board sample (6A), the board surface using an optical microscope (6B) and by SEM (6C, D). Visually, the color of the binderless boards ranges between light- to dark-brown, depending on the pressing temperature. Fig. 6B clearly shows that the shells (dark-brown) are surrounded by kernel materials (light brown), confirmed by SEM, Fig. 6C. Under the pressing conditions, particularly at higher temperatures and higher water contents, the various structures are less clearly visible, Fig. 6D.

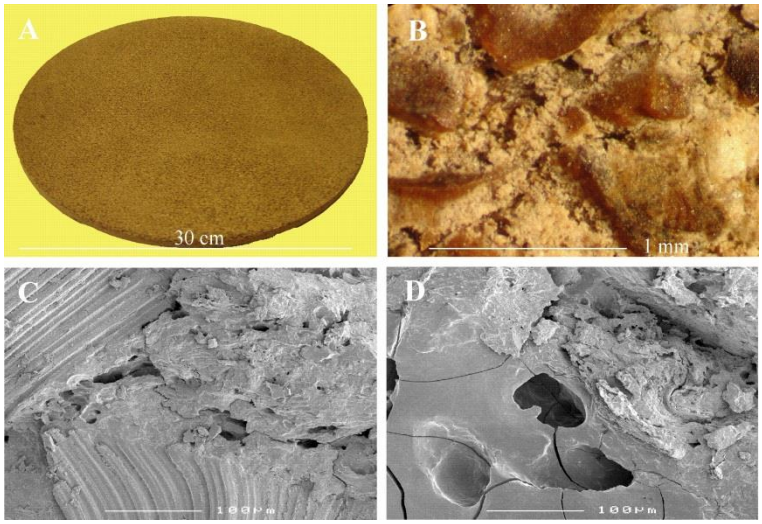

Figure 6. SEM pictures for a typical binderless board of de-oiled seed cake (A) Overall view, (B) Board surface using an optical microscope, (C) and (D) SEM images of the surface structure

2.3.6.1. TG/DT analysis of particle boards

The effect of pressing temperature on the DT profile of the binderless board samples is shown on Fig. 7. The DOSC feed is included as a reference. The DT profile of the binderless boards is a function of the processing temperature. Both the onset temperature and peak temperature for the first peak of the sample are shifted to higher values when increasing the processing temperature of the binderless boards. For instance, the feed material (DOSC) started to decompose at 180°C, whereas decompostion of the pressed board at the highest temperature in the range was above 200°C. Complete decomposition of boards occurs before 600°C, which is substantially lower than found for crude DOSC (620°C). The data indicates that chemical reactions occur in the boards at all pressing temperatures, even below the exothermic temperature peak observed in DSC analysis, Fig. 4. This is likely caused by differences in heating up times and holding times in the hot press and the DSC device.

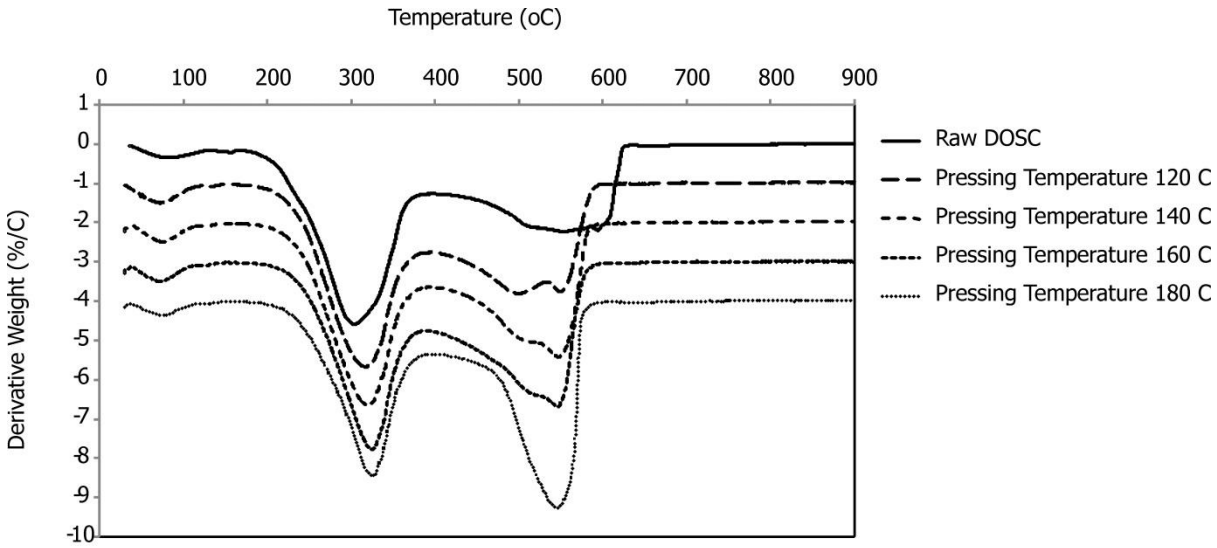

Figure 7. DT analysis of board materials from de-oiled seed cake at different processing temperature (10 MPa, 45/15 min/min, MC 10%)

2.3.6.2. Effects of DOSC moisture content and pressing conditions on binderless board properties

A total of 18 experiments were performed to gain insights in the effects of processing conditions and moisture content of the DOSC feed on mechanical properties of the binderless boards produced. For all experiments, the same batch of DOSC was applied. The following variables were investigated: water content of the feed material (5–20 wt%), pressing temperature (120–200°C), pressure (5–15 MPa), and heating time (30-60 min). The flexural modulus (M, GPa) and strength (S, MPa) were used as performance indicators for the boards produced.

Preliminary experiments with pressure variation (5, 10 and 15 MPa) at otherwise similar conditions showed that the mechanical properties of the boards were poor at low pressures whereas operational issues were encountered at high pressure (15 MPa). In the latter case, the particles were ejected from the mould. Therefore, the pressure was kept constant in the next set of experiments at 10 MPa. An overview of the experiments is given in Table 4.

The data were analyzed using non-linear multivariable regression and the results will be discussed for both responses (modulus and strength) separately. The modulus (M) is a clear function of the moisture content (MC) and the pressing temperature. The pressing time is statistically not significant, indicating that the lowest pressing time (30 minutes) is already sufficient. The model equation for the M is given in eq. 2.

Table 4. Overview of experiments for binderless board production

No.	Moisture Content (%)	T (°C)	P (bar)	t (min)	M (GPa)	S (MPa)
1	5	120	100	45	4.0	10.7
2	7.5	140	100	45	4.3	18.8
3	10	120	100	30	3.4	12.8
4	10	120	100	45	4.7	18.0
5	10	120	100	60	4.1	15.4
6	10	140	100	30	4.1	14.5
7	10	140	100	45	5.1	22.8
8	10	140	100	60	4.5	17.0
9	10	160	100	30	3.3	16.9
10	10	160	100	45	4.8	21.0
11	10	160	100	60	2.9	13.5
12	10	180	100	45	2.5	9.5
13	10	200	100	30	1.1	3.9
14	10	200	100	45	0.8	3.2
15	15	120	100	45	2.6	12.7
16	15	140	100	45	2.9	15.8
17	20	120	100	45	1.2	10.5
18	20	140	100	45	0.6	6.3

$$M = -11.20142 + 0.39841\,MC + 0.20677\,T - 0.024349\,MC^2 - 7.69336 \times 10^{-4}\,T^2 \quad (2)$$

Agreement between model and experimental data points is satisfactory (Table 5) and confirmed by a parity plot with experimental and modelled data (Fig. 8).

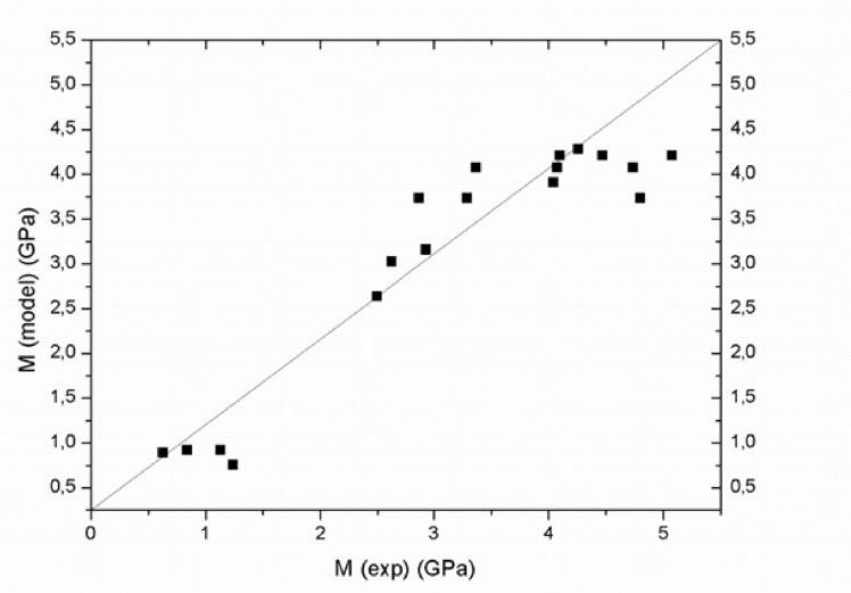

Figure 8. Parity plot for the binderless board flexural modulus showing experimental and model points

Table 5. Analysis of variance for the models for the flexural modulus and strength

	Modulus (M)	Strength (S)
F	23.4	63.4
P	< 1E-5	< 1E-5
R^2	0.87	0.87
R^2, adjusted	0.84	0.76
R^2, press.	0.78	0.60

A graphical representation of the effect of T and MC on the M of the board is given in Fig. 9. A clear optimum for M (4.3 GPa) is present within the design window for an MC of about 8 wt% and a pressing temperature of about 135°C. Higher moisture contents and temperatures have a strong negative effect on M. It is well possible that water acts to promote bonding via van der Waals forces by increasing the contact area of the particles, and via capillary sorption between particles. In the presence of heat, water can induce a wide range of physical and chemical changes (such as thermal softening of biomass, denaturation of proteins, and gelatinization of polysaccharides). These physico-chemical changes affect binding properties of the biomass particles. At higher moisture content (> 8%), the cell structure remains largely intact due to the incompressibility of wet biomass particles resulting in lack of coherence of biomass particles [37].

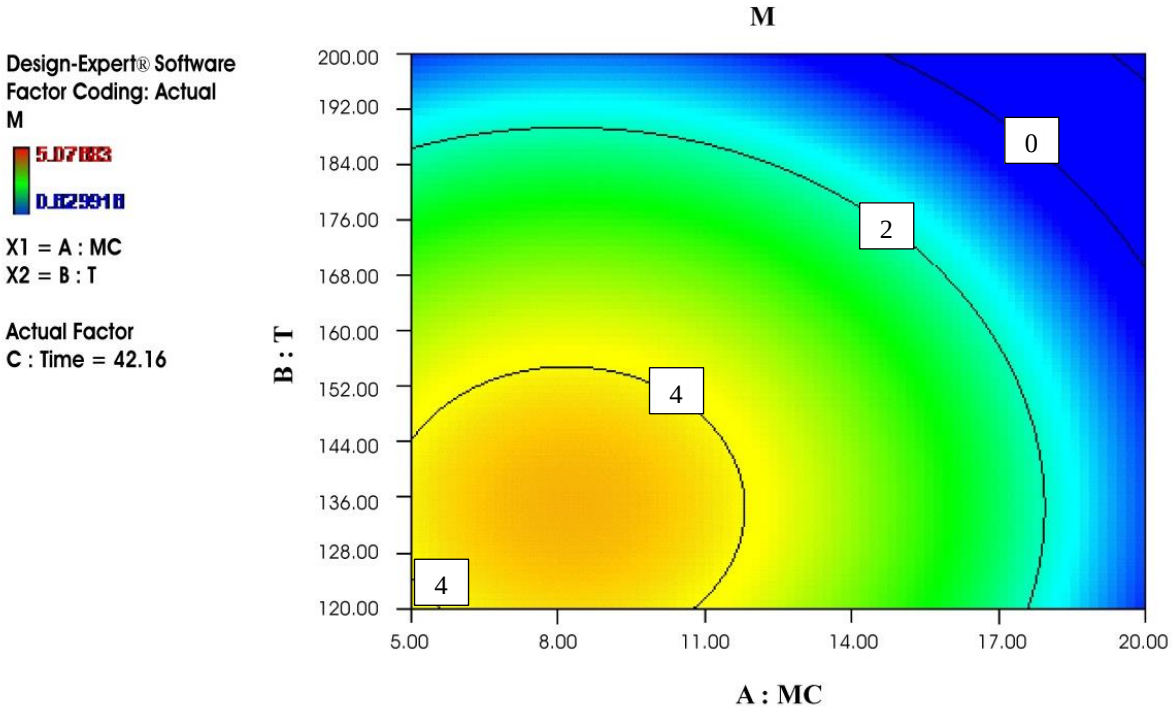

Figure 9. Effect of T and MC on the M values (GPa) of the binderless boards

A similar analysis was performed for the strength (S) of the binderless board. The model data are given in Table 4. Like the M, an optimum for the S with values exceeding 20 MPa was found within the design window, though the optimum is less steep than for M.

A comparison of the flexural properties of the DOSC boards with commercial boards is given in Fig. 10. It shows that the DOSC boards have lower flexural strength than commercial plywoods and MDF (medium density fiber boards), but higher than particle boards (thickness 8 mm). On the other hand, the flexural modulus of DOSC board is lower than plywood (5 mm) but higher than other products as shown in Fig. 10.

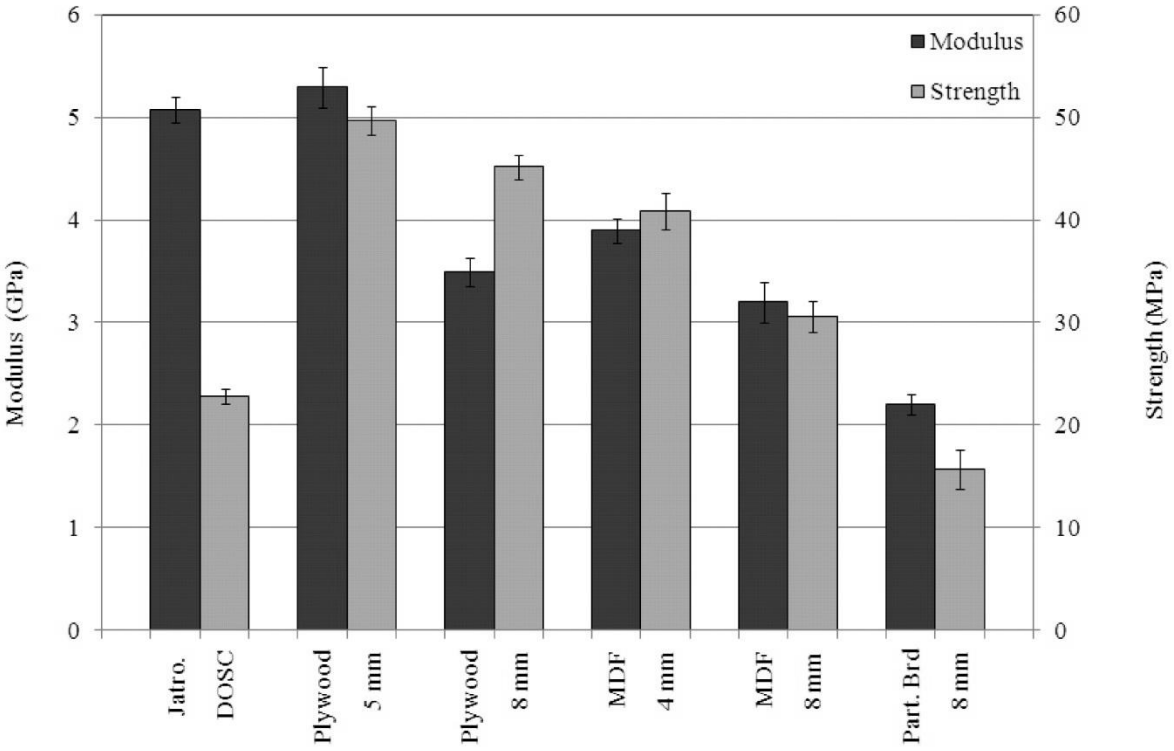

Figure 10. Flexural modulus and strength comparison of boards from de-oiled seed cake (140°C, 100 bar, heating time 45 min and MC 10 wt%) and relevant commercial boards

Addition of hemp woody core particles on the DOSC boards gave a small synergistic effect on the flexural properties,with an optimum of 50% hemp particle addition, see Fig. 11 for details.

2.3.6.3. Water absorption and thickness swelling

The effect of water on flexural modulus and strength of the binderless board (140°C, 10 MPa, and a pressing time of 45 min with a MC of 10%) using a standardized procedure (24 h at room temperature) is shown in Fig. 12. Clearly, the mechanical

properties of the binderless board deteriorate after soaking in water i.e. from 5.1 to 0.3 GPa for the modulus and from 22.8 to 3.8 MPa for strength.

The water absoption and swelling of the DOSC binderless board produced at an optimum temperature are 74% and 19% respectively, see Table 6 for details. The water absorption and thickness swelling values are much higer than for MDF based commercial boards but comparable with commercial particle board.

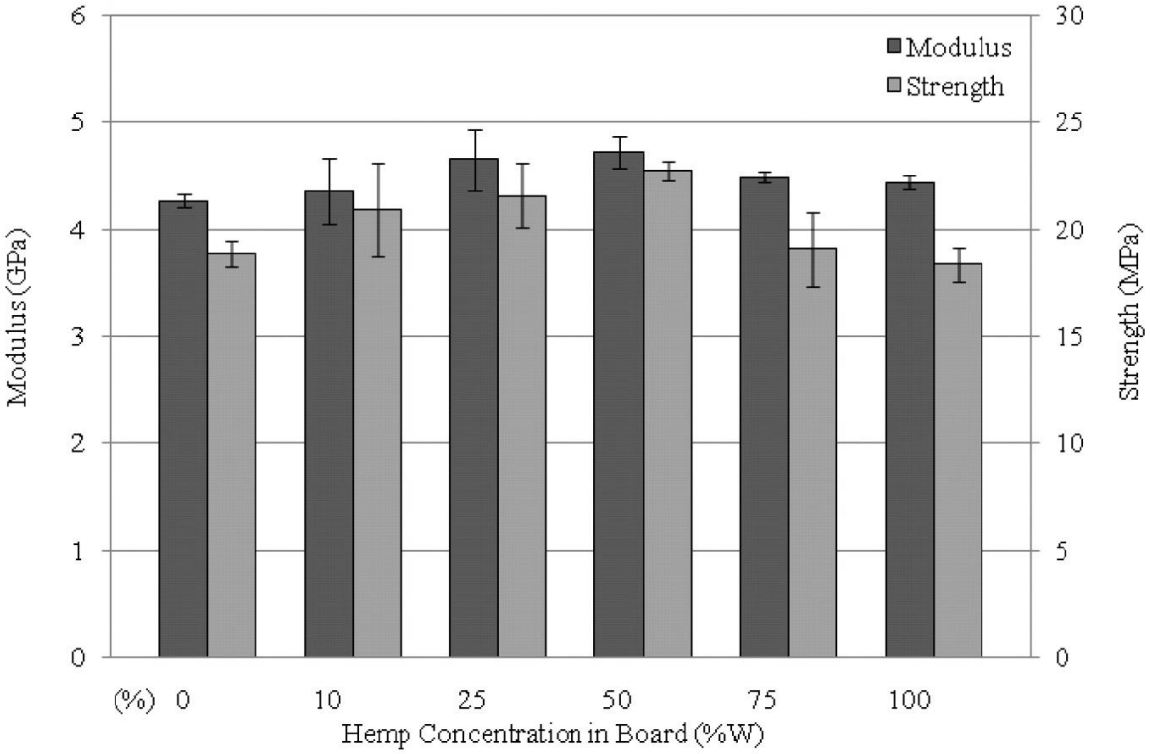

Figure 11. Effect of hemp addition on flexural modulus and strength of particle board (boards prepared at 140°C, MC of 7.5 wt% and heating/cooling times of 45/15 min)

Table 6. Water absoption and thickness swelling of binderless board prepared in this study[a]

	Water Absorption (%)	**Thickness Swelling (%)**
DOSC binderless board from de-oiled seed cake	74	19
Commercial particle board [b]	65	21
Commercial MDF[b]	24	17
Coir binderless board [b]	7.5-9.5	7.6-10.9

[a] binderless board from DOSC were prepared at 140°C, 10 MPa, and a heating time of 45 min, MC was 10%; [b] Snijder, *et. al.*, 2006 [41]

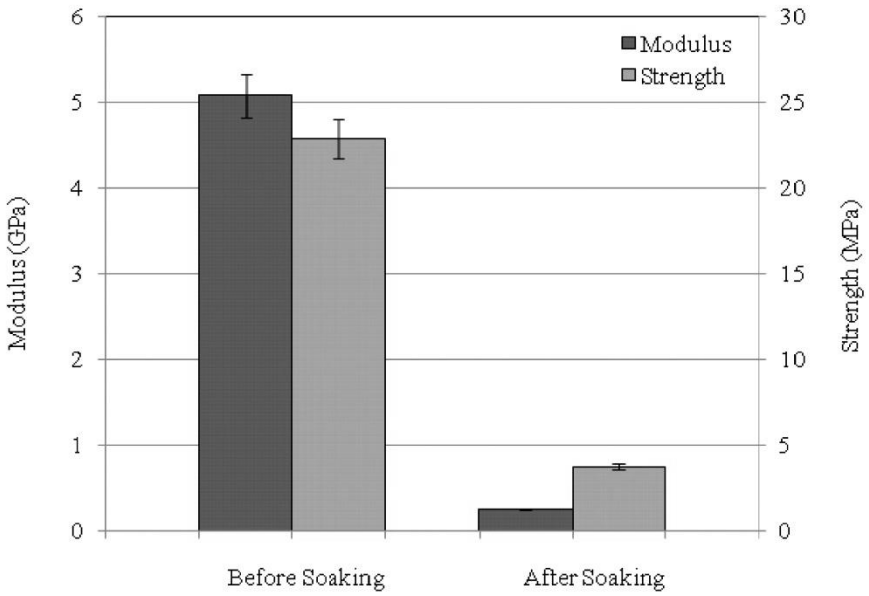

Figure 12. Effect of soaking on flexural modulus and strength of binderless board (prepared at 140°C, 10 MPa, heating/cooling time of 45/15 min, MC of 10 wt%)

2.4. Conclusions

The composition of various parts of *Jatropha curcas* L. (JCL) seeds before and after oil expelling was determined. The potential of the de-oiled seed cake obtained by mechanical pressing of the seeds (shell and kernel) followed by de-oiling with hexane for the preparation of binderless boards was explored. The de-oiled press cake contains a considerable amount of proteins, lignin and cellulose/ hemicellulose. The thermal behavior of the Jatropha seed cake samples indicated the occurrence of irreversible chemical cross-linking reactions between 40 and 185°C. These reactions are important and provide the basis for the production of binderless boards without using additional adhesives.

Binderless boards were prepared at different operating conditions and best mechanical product properties were obtained at 8 wt% moisture content, a pressing temperature at 135°C, 10 MPa pressure, and heating and cooling times of 30 and 15 min, respectively. Relevant (mechanical) properties of the boards are comparable with commercial particle boards obtained with urea-formaldehyde formulations, though considerably lower than for typical MDF boards. The addition of hemp fibers to the formulation resulted in a small though significant positive effect on mechanical properties and an optimum formulation with 50 wt% hemp was determined. Further product development activities including determination of relevant processing and product properties other than mechanical ones will be required to assess the commercial potential of the binderless boards prepared.

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List of abbreviations

DOSC : de-oiled seed cake
DOSK : de-oiled seed kernel
DOSS : de-oiled seed shell
JCL : *Jatropha curcas* Linnaeus
MC : moisture content (wt%)
M : modulus (GPa)
S : strength (MPa) .

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Chapter 3

Catalytic Liquefaction of *Jatropha curcas* L. Seed Cake

H. Hidayat, U. Prijanto, J.E.G. van Dam, and H.J. Heeres

Abstract

The catalytic liquefaction of *Jatropha curcas* L. seed cake obtained after oil-pressing into value-added products was investigated. The experiments were carried out in a batch autoclave at 5 MPa (initial) hydrogen pressure in four different solvents (water, ethanol, acetone, tetraline, 30 wt% DOSC) at a temperature of 300°C (30 min reaction time) in the absence and presence of catalysts (limonite or sodium carbonate). The liquid products were fractionated by vacuum distillation and relevant properties of each fraction were determined. Experiments in ethanol gave the highest seed cake conversion and oil yield, both in the presence and absence of a catalyst. The presence of a catalyst in combination with hydrogen had a beneficial effect on oil yield and best results were obtained using the limonite-sulfur catalyst (46 wt% oil yield). The oils obtained in ethanol in the presence and absence of the Fe-limonite catalyst were analyzed in detail using elemental analysis, GPC, GC-MS and ^{1}H NMR.

3.1. Introduction

Environmental concerns and the increasing demands for fossil resources have boosted research and development activities on renewable resources [1-5]. Of particular interest is the use of biomass, the only renewable source for carbon derived transportation fuels and biobased products. A wide range of technologies is available for such conversions. In general, the technologies can be divided into thermochemical processes (gasification, pyrolysis and liquefaction) and low temperature processes (hydrolysis, fermentation, anaerobic digestion).

Hydrothermal liquefaction is a well-known conversion technology for the liquefaction of wet biomass sources [6-9]. The process is typically carried out in water at temperatures between 280 and 370°C and pressures between 10 and 25 MPa. In the process, water is not only a solvent but also acts as a reactant (for instance for the depolymerization of carbohydrates to low molecular weight sugars) and catalyst. The main advantage of hydrothermal liquefaction is that the energy consuming of biomass drying step is not required, as is the case for gasification and pyrolysis processes. The main products are a liquid rich in organics, also known as an organic biocrude, an aqueous phase containing the hydrophilic organics, a gas phase and char. Besides studies using various biomass sources, extensive studies have been carried out with model components, for example carbohydrates (cellulose, hemicellulose, starch, low molecular weight carbohydrates), lignin and lipids [7].

Catalysts have a profound effect on liquid yields and composition [10-15]. Both homogeneous, and particularly alkali salts like metal carbonates, and heterogeneous catalysts have been explored. One of the functions of the catalysts is to enhance biomass gasification rates to CO and hydrogen. Hydrogen may act as a reducing agent and as such leads to an increase the H/C ratio of the product oil. Though gasification suppresses the liquid yields, it has a positive effect on the deoxygenation level of the product and as such on the higher heating value (HHV) of the biocrude. Examples of heterogeneous catalyst are supported Ni, Pd and Pt catalysts. Iron based catalysts such as FeS and $FeSO_4$ have also been reported and are advantageous when considering the price of the catalysts [13,16]. At elevated temperatures and in the presence of sulfur, iron based catalysts will transform into pyrrhotites ($Fe_{1-x}S$) with FeS_2 as an intermediate. The presence of small amounts of Ni in the catalyst is reported to have promotional effect on the liquefaction activity [17].

Biomass liquefaction in water has been studied in detail [7,12,18,19]. Several other solvents than water have also been explored, examples include alcohols, acetone, benzene, n-pentane, toluene, tetralin, phenol, ethylene glycol, glycerol, acetic acid and combinations of these solvents with water [13,20-26]. The solvent greatly affects not only the biocrude yield but also the liquid composition.

The gas phase composition has a profound effect on conversion and product yield. Wang*, et. al.* (2007) demonstrated that the addition of hydrogen gas during the liquefaction of sawdust resulted in improved product yields compared to syngas, Ar or

CO [11]. The presence of hydrogen gas during biomass liquefaction not only increases feed conversion and biocrude yield but also has a positive effect on the quality of the biocrude product [13]. The role of hydrogen has been postulated and it is thought to play a role in the depolymerization process by e.g. promoting hydrocracking reactions, and reduces char formation by hydrogenation of reactive molecules that are prone to re-polymerization [27].

Recently, first studies on the use of protein rich biomass feedstocks, also known as proteinaceous biomass, as feeds for hydrothermal liquefaction have been reported. Examples are the use of aquatic biomass sources like algae and seaweed. Typical biocrude yields are in between 5 and 55%, and these were shown to be a function of process conditions and also the fatty acid contents of the samples. A considerable amount of the bound nitrogen is converted to low molecular weight nitrogen containing organics that end up in the biocrude. The elementary composition of the oils ranges from 46 to 84% carbon, 5 to 15% hydrogen, 1 to 7% nitrogen and 0 to 25% oxygen, HHV were in between 23 and 50 MJ/kg [28-33]. Another example of a nitrogen rich biomass feed involves the liquefaction of dried distillers grains with solubles (DDGS), a residue from ethanol fermentation processes [34,35].

Here, we report our studies on the liquefaction of a typical proteinaceous biomass i.e. the *Jatropha curcas* L. (JCL) seed cake (SC). To the best of our knowledge, seed cake valorization by (hydro-) thermal liquefaction has not been reported to date and as such is an absolute novelty of this chapter. The effects of solvents (water, ethanol, acetone and tetraline) and catalysts (sodium carbonate as an example of a homogeneous catalyst and Fe-limonite in combination with sulfur as an example of a heterogeneous catalyst) on the feed conversion, biocrude yield and physical and chemical properties of the liquefied oils were determined.

3.2. Experimental

3.2.1. Materials

JCL seed cake (SC) was obtained by pressing *Jatropha curcas* L. seeds in a processing unit at B2TE – BPPT Indonesia. The SC was stored at 4°C to inhibit the growth of fungi. Before use, the residual amounts of oil were removed by a solvent extraction with n-hexane in a soxhlet set-up for 8 h. The de-oiled *Jatropha* Seed Cake (DOSC) sample was subsequently pulverized, sieved through a 60-mesh (240 μm) screen, and dried at 70°C in a vacuum dryer.

Four different solvents were used, i.e. water (aquabidest), ethanol 99.8% (Merck), acetone 98% (Merck), and tetralin (1,2,3,4-tetrahydronaphthalene 99%, Sigma Aldrich). Limonite ore was obtained from the nickel mine of PT Inco in Soroako, Sulawesi Island, Indonesia and Na_2CO_3 from Wako Pure Chemical Industries Ltd. The elemental composition of the limonite catalyst was determined by inductive coupled plasma (ICP) spectroscopy and the results are shown in Table 1. The remaining

elements are H and O. Before use, the limonite was pulverized in water to an average particle size of about 0.5-0.8 μm using a batch-type agitated beads mill (Eirich Tower Mill, 6 L) at 1000 rpm for 3 h. The resulting limonite slurry was dried at 105°C until constant weight. Sulfur powder (purity 98.0%) was obtained from Wako Pure Chemical Industries, Ltd.

Table 1. Composition of the limonite catalyst

	Limonite composition (wt%, dry)									
Element	Na	Ca	Mg	Al	Si	Cr	Co	Fe	Ni	S
Concentration	0.04	0.00	0.08	3.35	2.64	0.81	0.09	46.96	1.29	0.04

3.2.2. Proximate, ultimate analysis and heating value of raw materials

The proximate analysis of DOSC were performed using a LECO TGA 501 thermogravimetric analyzer. The moisture content of DOSC was performed according to ASTM E871 – 82(2006), the ash content using ASTM D1102 – 84(2007) and the volatile matter content using ASTM E872 – 82(2006). The ultimate analysis were performed on a LECO CHN-100 analyzer for carbon, hydrogen and nitrogen (ASTM E777 and A778) and an SC-32 analyzer for total sulfur (ASTM E775). The oxygen content was determined as difference. The heating value of DOSC was performed using an AC500 Isoperibol Calorimeter from LECO.

3.2.3. Liquefaction experiments

The liquefaction experiments were performed in a batch autoclave (1 L), see Figure 1 for details. The reactor was equipped with a magnetic stirrer and heating mantle.

Before each experiment, the reactor was purged three times with nitrogen gas followed by hydrogen gas (three times) at room temperature to remove air. Subsequently, a leakage test was performed by pressurizing the reactor to 20 MPa with hydrogen gas at room temperature for at least 12 h. The reactor was charged with DOSC (80 g), solvent (160 g) and, when appropriate, a catalyst. For the limonite catalyst, 1.0 wt% intake on DOSC (dry-ash free basis, daf) was applied and the appropriate amount of sulfur was added to obtain an atomic S to Fe ratio of 2 [17]. For Na_2CO_3, 5.0 wt% intake on DOSC (daf) was used [36]. Subsequently, the reactor was pressurized with 5 MPa of hydrogen at room temperature, the reactor was closed and heated to 300°C using a stirring speed of 500 rpm. The temperature and the stirrer speed were monitored and controlled, the pressure versus time was also recorded. Typically, a slight increase in pressure was observed during reaction. After 30 min at 300°C, the reactor was cooled to ambient temperature. The cooling time was approximately 1 h. The reactor was depressurized and the resulting liquid slurry was weighed and subjected to a vacuum distillation at 10 mmHg (ASTM D1160) into an aqueous fraction,

light organics (LO, b.p. <180°C), medium organics (MO, b.p. 180-300°C), heavy organics (HO, b.p. 300-420°C), and residue (b.p. >420°C). When ethanol or acetone were used as the solvent, the LO fraction was subjected to distillation in a rotary evaporator at 70°C to remove these low boiling solvents. Throughout this chapter, the LO fraction is designated as the light organic fraction after removal of the solvents. The amount of gas phase components after reaction was determined using a gas meter and used as input for mass balance calculations. The gas phase composition was analyzed by GC-FID and TCD. Most of the liquefaction tests were performed in duplicate and the reported product yields are the averaged values.

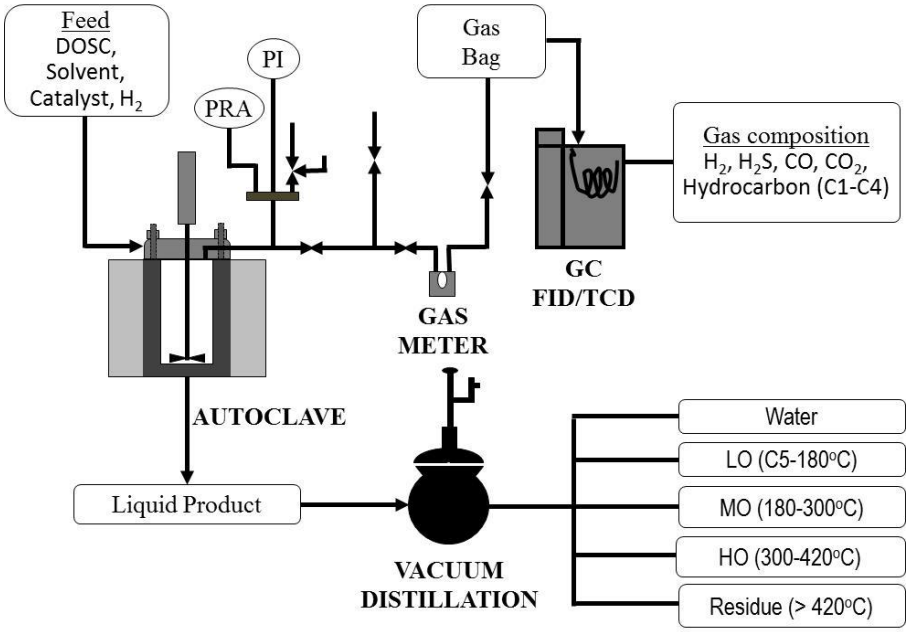


Figure 2. Schematic diagram of DOSC liquefaction testing

3.2.4. Gas phase analysis

The composition of the gas phases were analyzed using two different GC's. The H_2, CH_4, CO and CO_2 contents were quantitatively analyzed using a Shimadzu 2014 GC equipped with a thermal conductivity detector (TCD) and a dioctyl pthalate column (4 m x 3 mm) using argon as the carrier gas. The oven temperature was kept at 40°C. The C_1-C_4 hydrocarbons were analyzed using a Yanaco G2800GC equipped with a flame ionization detector (FID), a Porapak-Q column (2 m x 3 mm) and nitrogen as the carrier gas. The detector temperature was set at 140°C and a heating rate of 5°C/min was applied. A standard gas (PT. AGI, Indonesia) containing H_2, CH_4, CO, CO_2, C_2H_6, C_3H_8, i-C_4H_{10} and n-C_4H_{10} was used for peak identification and quantification. The concentration of H_2S was determined using a gas sampling pump (GASTEC Model GV 100S) and detector tube (No. 4HH).

3.2.5. Liquid phase analysis

3.2.5.1. Elemental composition, heating value and water content analysis

The elemental composition of the product oils (C, H, N and S) was determined using a Euro Vector 3400 Series CHNS-O analyzer, the oxygen content was determined by difference. The analysis was carried out in duplicate and the average value is reported. The higher heating values (HHV) of the oils were calculated using the Channiwala and Parikh (2002) relation (Eq. 1) where C, H, S, O, N and A represent carbon, hydrogen, sulfur, oxygen, nitrogen and ash content in mass percentages on dry basis [37].

$$\text{HHV}\ (MJ/kg) = 0.3491\ \text{C} + 1.1783\ \text{H} + 0.1005\ \text{S} - 0.1034\ \text{O} - 0.0151\ \text{N} - 0.0211\ \text{A} \quad (1)$$

The water content of the samples was determined using Karl Fischer titration with a Metrohm Titrino 758 titration device. A small amount of oil sample (± 0.10 g) was added to an isolated glass chamber containing hydranal (Karl Fisher solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant composit 5K (Riedel de Haen). All measurements were conducted in duplicate and the average value is reported.

3.2.5.2. GC-MS analysis

GC-MS analysis were performed on a Quadrupole Hewlett Packard 5972 MSD attached to a Hewlett Packard 5890 GC equipped with a 30 m x 0.25 mm i.d. and 0.25 μm film sol-gel capillary column. The injector temperature was set at 250 °C. The oven temperature was kept at 40°C for 5 minutes then heated up to 250 °C at a rate of 3 °C min^{-1} and then held at 250 °C for 10 minutes. Before analysis, solids in the liquid sample were removed by filtration using a plastic syringe equipped with PTFE membrane. Samples were injected after dilution using an internal standard solution (di-n-butylether (DBE) in THF).

3.2.5.3. GPC and ^{1}H NMR analysis

The molecular weights and molecular weight distributions of the product oils were determined by gel permeation chromatography (GPC) with a system consisting of a Hewlett Packard 1050 pump, a 410 differential refractometer and three thermostated (35 °C) Shodex KF columns in series. THF (0.55 mL/min) was used as the mobile phase and a pressure of 140 bar was applied. The column was operated at 40°C. An injection volume of 25 μl with a sample concentration of about 1.0 g/L was applied. Calibration was performed using polystyrene standards of known molecular weight and narrow molecular weight distribution.

The ^{1}H NMR spectra were recorded on a 500 MHz NMR (Varian). The samples were filtered over $MgSO_4$ powder to reduce the water content and subsequently dissolved in $CDCl_3$.

3.2.6. Definitions

Product yields (on weight basis) were calculated as follows:

$$\text{LO yield} = \frac{\text{LO from distillation}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (2)$$

$$\text{MO yield} = \frac{\text{MO from distillation}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (3)$$

$$\text{HO yield} = \frac{\text{HO from distillation}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (4)$$

In case of ethanol and acetone, it is assumed that these solvents end up in the LO fraction after distillation as their boiling points are in the range of LO fraction. The actual reported LO yield for these solvents is the isolated LO yield minus the solvent intake. A similar procedure was applied for tetralin, assuming that this solvent ends up in the MO fraction (b.p. 180-300°C).

The other product yields (wt% on DOSC intake) were calculated as follows:

$$\text{Gas yield} = \frac{\text{Amount of gas from the process} - \text{Intake } H_2}{\text{daf DOSC intake}} \text{ x } 100\% \quad (5)$$

$$H_2O \text{ yield} = \frac{\text{Amount of water phase after distillation} - H_2O \text{ (in DOSC + solvent + catalyst)}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (6)$$

$$\text{Residue} = \frac{\text{Solid residue after distillation} - \text{Ash (in DOSC +catalyst)}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (7)$$

$$H_2 \text{ yield} = \frac{\text{Amount of } H_2 \text{ in the reactor after reaction} - H_2 \text{ feed}}{\text{daf DOSC intake}} \text{ x } 100\% \quad (8)$$

The DOSC conversion was determined from the DOSC intake and the residue after distillation according to the following equation:

$$\text{DOSC Conversion} = \frac{\text{daf DOSC intake} - \text{Residue}}{\text{daf DOSC intake}} \text{x } 100\% \quad (9)$$

Typical mass balance closures for the experiments were between 90-95%. Losses are mainly due to partial evaporation of the volatile fraction in the distillation procedure.

The energy recovery of the liquefaction process was determined from the mass and HHV values of the product oil and DOSC feed according to the following equation:

$$\eta = \frac{HHV_{product\ oil} \cdot\ mass\ product\ oil}{HHV_{DOSC} \cdot\ daf\ DOSC\ intake} \quad (10)$$

3.3. Results and discussion

3.3.1. De-oiled seed cake analysis

The de-oiled *Jatropha* seed cake (DOSC) obtained from mechanically expelling Jatropha seeds followed by removal of residual oil using a hexane extraction mainly consists of polysaccharides (cellulose and hemicellulose, 33 wt%), proteins (28 wt%) and lignin (29 wt%) [38]. An overview of the relevant characteristics of the DOSC is given in Table 2. Of relevance for the liquefaction research described here on dry-basis is the ash content of 9.5 wt%, mostly in the form of minerals such as potassium, calcium, and magnesium [39].

Elemental analysis shows high nitrogen content (3.3 wt%) due to the presence of proteins [40]. The atomic H/C ratio is 1.5, and the oxygen to carbon ratio (O/C) is 0.7, which is in the broad range reported for (lignocellulosic) biomass [41]. The sulfur content of DOSC (0.5 wt%) is higher than reported for typical woody biomass sources [42]. However, for the limonite catalyzed liquefaction reaction, sulfur is required for an improved catalytic activity, and as such the presence of S is not by definition a disadvantage [43].

Table 2. Relevant characteristics of DOSC

Analysis	Component	Dry basis
Proximate (wt%)	Moisture	-
	Volatile Matter	51.0
	Fixed Carbon	39.5
	Ash	9.5
Ultimate (wt%)	Carbon	41.7
	Hydrogen	5.3
	Nitrogen	3.3
	Oxygen (by diff.)	39.5
	Sulfur	0.5
HHV(MJ/kg)		16.6

3.3.2. Non-catalytic liquefaction experiments

The non-catalytic liquefaction of DOSC was studied in four different solvents: water, ethanol, acetone and tetralin (1,2,3,4-tetrahydronaphthalene), the latter being a

potential hydrogen donor solvent. The experiments were performed in the presence of hydrogen (5 MPa of initial hydrogen pressure) at 300°C for a reaction time of 30 min (excluding heating and cooling). After reaction, a slurry was obtained, which was subjected to fractionation by vacuum distillation (ASTM D1160). Generally, three liquid fractions were obtained, a light organic fraction, a clear-brown medium organic fraction (MO), a dark-brown heavy organic fraction (HO), and a black solid residue. Upon standing, the light fraction separates into a clear-yellowish water phase and a light-brown light organic fraction (LO), In addition, gas phase components like CO, CO_2, CH_4, C_2H_6, C_3H_8, C_4H_{10} and H_2S were formed. The product fractions for each solvent were quantified and the results are shown in Figure 2. For clarity, the LO, MO and HO yields are summed up and denoted as distillate.

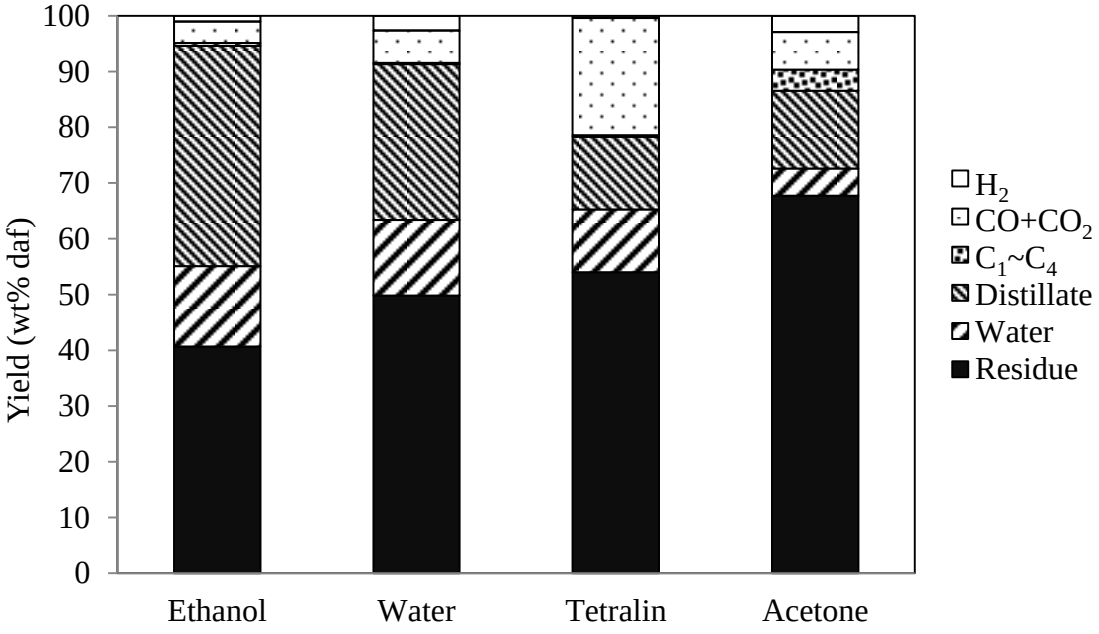


Figure 2. Effect of solvent type on the product yield for non-catalytic DOSC liquefaction

Clearly, the solvent has a major effect on the yields of the various product fractions. Ethanol resulted in the highest DOSC conversion (60 wt%), followed by water (50%), tetralin (46%) and acetone (32%). Systematic studies on solvent effects in biomass liquefaction studies, and particularly for protein rich biomass sources, have not been reported in great detail to date, making comparison with literature data difficult. Solvent studies by Liu and Zang (2008) using pinewood at 300°C in batch showed that water led to the highest conversion followed by ethanol and acetone, though the differences were in a relatively narrow range (30-40%) [23]. However, process conditions for both studies are different (longer reaction times and the presence of hydrogen in our case), making comparison rather difficult.

The total organics yield (distillate in Fig. 2) also shows a strong solvent dependency. Ethanol gave the highest yield (40 wt%), followed by water (28 wt%), acetone (14 wt%) and tetralin (13 wt%). Positive effects of the use of alcohols as the

liquefaction solvent on oil yields have been reported in the literature for various biomass sources. For instance, Yuan *et. al*. et al (2007) showed that the addition of ethanol to water gave a positive effect on the oil yields for the uncatalyzed liquefaction of rice straw [12]. Yield increase from 28 to 38 wt% was reported when changing the solvent from pure water to an ethanol-water mixture (1 to 1 volume ratio) at 264°C. The low organic product yields for tetralin are mainly due to the formation of large amounts of gas phase components (Figure 2). Apparently, gasification is strongly promoted in this solvent, presumably by gasification of light organic products [20]. The high LO amount formed in tetraline compared to other solvents confirms this observation (Figure 3).

Considerable amounts of water are formed during the liquefaction reaction, see Figure 2 for details. This is a well-known feature of biomass liquefaction processes and is due to subsequent dehydration reactions of monomers or oligomers formed after the initial depolymerization of the biomass components and likely also by hydrodeoxygenation reactions. Water formation levels are, as expected, solvent depending, with solvents giving higher liquid product yields also lead to the formation of larger amounts of water. Yield and composition of the gas phase after reaction are a function of the solvent, see Figure 2 for details. The major gas phase components are CO and CO_2 (CO_x), while only minor amounts of C_1-C_4 hydrocarbons are formed. Hydrogen consumption is negligible and actually hydrogen mass balance calculations indicate that some hydrogen is formed during reaction (< 3%). A possible explanation is the occurrence of the water gas shift reaction.

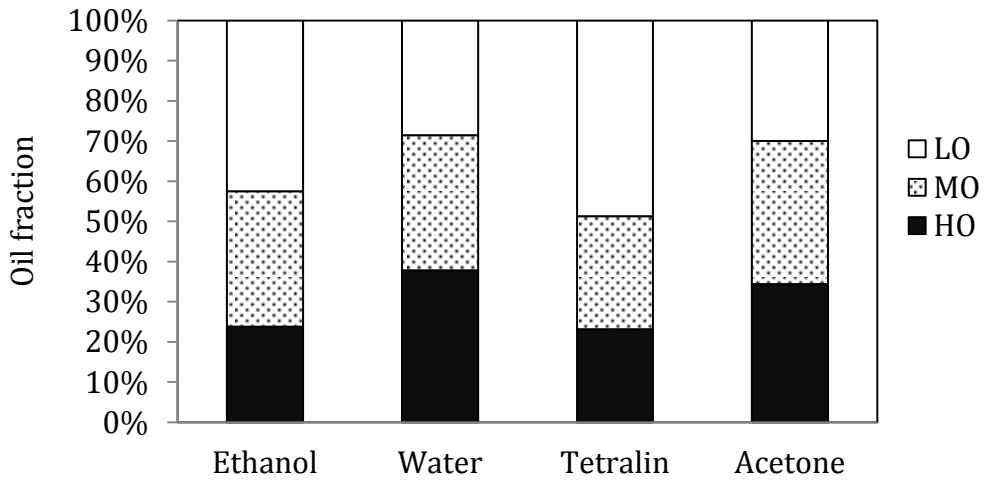


Figure 3. Effect of solvent type on distribution of product fractions for non-catalytic liquefaction

The effect of the solvent type on the amounts of the individual distillation fractions is given in Fig. 3. Tetralin and ethanol gave the highest amounts of LO (45 - 50%), followed by acetone and water. Apparently, molecular weight breakdown of the biopolymers is more effective when using these solvents. When aiming for a high LO yield, the use of ethanol is advantageous, as in tetralin the total biocrude oil yield is

lower than for ethanol. In addition, ethanol may be obtained from renewable resources and is easily removed from the product by distillation due to its lower boiling point compared to tetralin.

3.3.3. Effects of catalysts on biocrude yield and product fractions

The effect of a catalyst in the form of an Fe based limonite ore on the liquefaction process for all four solvents was explored. This catalyst is commonly used in coal liquefaction [44-46] and contains nearly 50 wt% of Fe (Table 1). Major components are α-FeOOH (geothite) and α-$Al(OH)_3$ (gibbsite) [17]. A small amount of sulfur was added (S to Fe molar ratio of 2) to activate the catalyst. Reactions were performed in a batch set-up with conditions similar as those for the non-catalytic experiments. The results for the experiments are given in Figure 4. The presence of the limonite-sulfur catalyst significantly enhanced the conversion of DOSC in all solvents used. For ethanol, the best solvent for the non-catalytic liquefaction, the DOSC conversion increased from 59 wt% to 74 wt%. In line with this finding is a significant increase in the total biocrude yield for all solvents. Highest biocrude yields were again observed for ethanol, where a yield increase from 40% for the non-catalytic to 46% when using the limonite catalyst was observed.

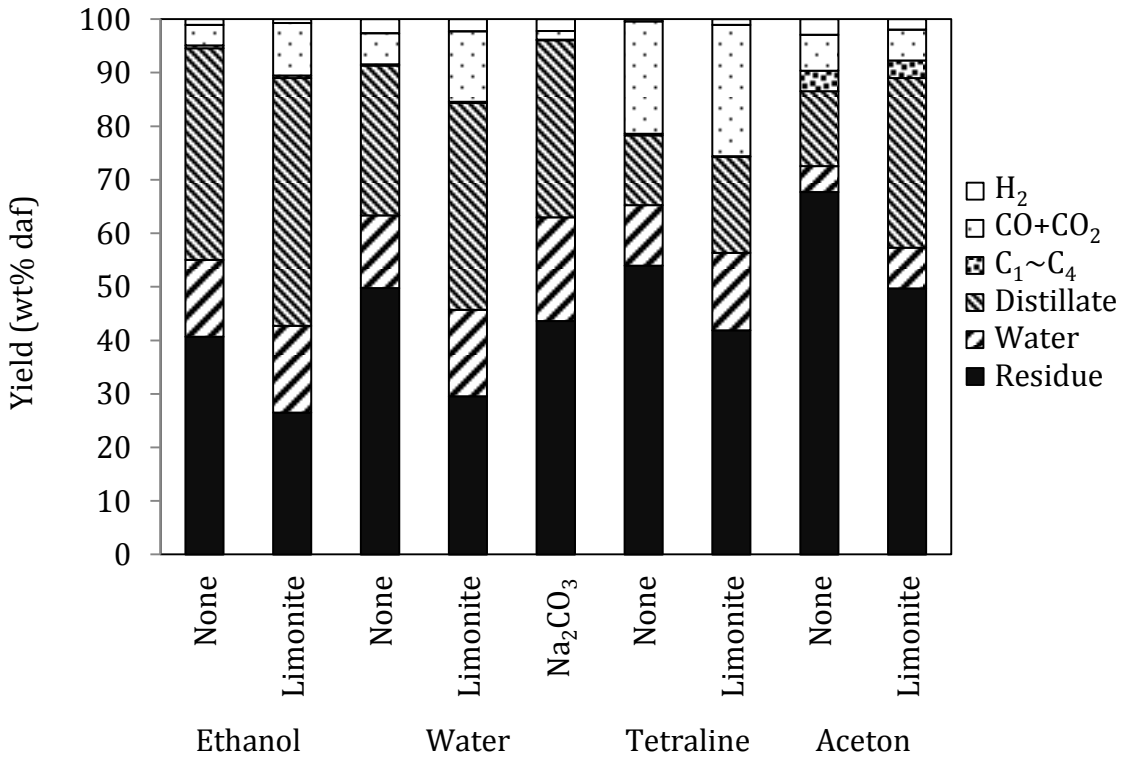


Figure 4. Effect of catalyst addition on product distribution of DOSC liquefaction for different solvents

Furthermore, the use of Na_2CO_3 as a catalyst was probed for the liquefaction in water. Positive results were obtained and the oil yield increased from 28% to 33%.

Alkaline salts, such as sodium carbonate and potassium carbonate are known to have a beneficial effect on biomass liquefaction yields in water [7,19,36,47]. In our study, the biocrude yield for Na_2CO_3 is lower than for the limonite catalyst. This indicates that limonite catalysts have good potential for the (hydrothermal) liquefaction of biomass.

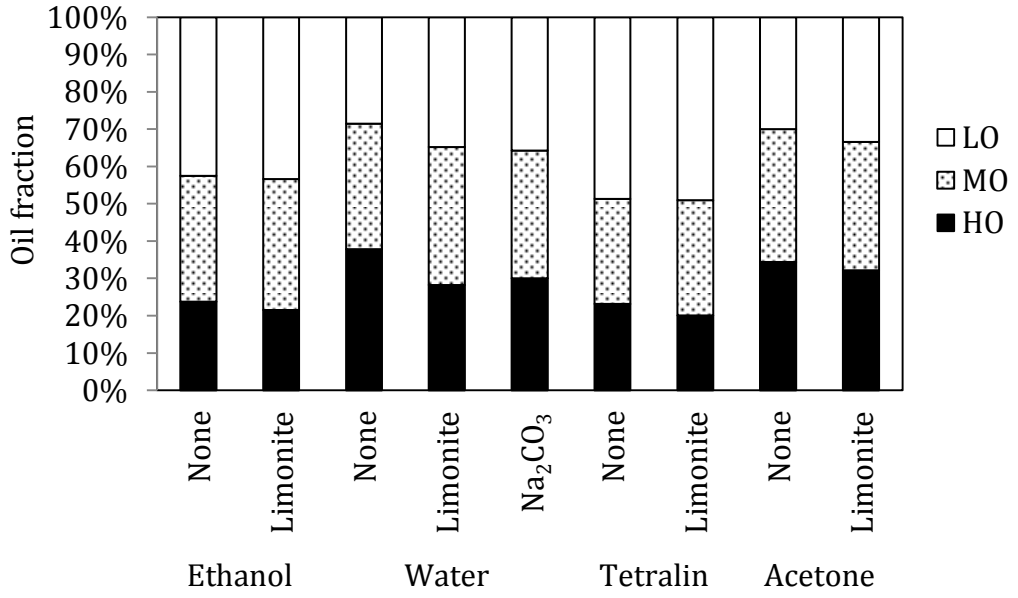


Figure 5. Effect of catalyst addition in different type of solvent on oil fraction of DOSC liquefaction

The effect of catalyst addition on the relative ratios of the various oil fraction for all solvents is given in Fig. 5. The presence of a catalyst did not only significantly increase the oil yield, but also led to a small increase in the LO fraction, indicative for higher biopolymer de-polymerization rates when using a catalyst.

3.3.4. Product composition and properties for liquefactions in ethanol

Product composition and properties for the catalytic (Fe based) and non-catalytic liquefaction experiments in ethanol were determined in detail and including elemental composition of the various distillation fractions, molecular weight determinations by GPC and information about chemical composition by using NMR. The focus was on ethanol derived samples as this solvent showed best performance regarding biocrude yield.

Table 3 shows the elemental composition of the starting material (DOSC) and the product oils. The oils have a much higher carbon and hydrogen content and a reduced oxygen content compared to the feed. The lower oxygen content of the liquefied oils indicates that de-oxygenation occurs to a significant extent. This is due to dehydration reactions, formation of CO and CO_2 and likely also by hydrodeoxygenation reactions when using a catalyst (Figure 2 and 4). This observation corresponds well with the results reported in literature [12,13], showing that the oxygen content of the product

oils are always lower than the feed material. These trends in elemental composition are visualized in a van Krevelen plot in Figure 6. As a result of the lower O/C ratio, the HHV of the product oils (29-37 MJ/kg) are considerably higher than the feed (18.5 MJ/kg).

Table 3. Elemental composition and calorific value of the (DOSC feed Ana product oils using ethanol as the solvent

Element	DOSC	Without catalyst			With Fe based catalyst		
		LO	MO	HO	LO	MO	HO
C (wt%)[a]	46.1	64.8	65.1	69.9	71.0	70.6	77.0
H (wt%)[a]	5.9	8.0	7.1	7.6	9.1	8.7	8.8
N (wt%)[a]	3.7	9.1	10.0	9.8	9.5	10.7	10.0
S (wt%)[a]	0.6	0.3	0.2	0.1	1.3	1.1	0.5
O (wt%)[b]	43.7	17.8	17.6	12.6	9.1	8.9	3.7
HHV (MJ/kg)[c]	18.5	30.1	29.1	31.9	34.6	33.9	36.8

[a] On a moisture-ash free basis; [b] By difference; [c] Higher heating value were calculated using eq. 1.

Of particular interest are the large differences in elemental composition of the fractions for the catalytic and non-catalytic experiments (Table 3 and Figure 6). The use of the limonite-sulfur catalyst leads to products with a significantly lower oxygen content and thus O/C ratio. This is in agreement with the result reported by Huang, *et. al.* (2011) for *Spirulina* microalgae liquefaction in ethanol where the catalyst (FeS) enhanced hydrogen transfer reactions (hydrocracking and hydro-(deoxy-)genation reactions) leading to lower oxygen contents [48]. For instance, the carbon content of the biocrude increased from 69.4 to 76.2 wt% while the oxygen content decreased from 11.4 to 9.8 wt% when using FeS as the catalyst. Thus, the catalytic liquefactions using Fe-based catalysts not only lead to higher oil yield but also have a positive effect on the elemental composition and calorific value of the oil.

The nitrogen content of the liquefied oils is higher than that of the DOSC feed. Mass balance considerations imply that that the residue should be low in nitrogen. These observations indicate that the proteins in the feed are readily depolymerized and converted into low molecular weight, volatile components. This is supported by literature data on hydrothermal liquefaction model studies using proteins and amino-acids [18,19], which show that conversion rates for these components are high. Typical nitrogen containing components in liquefied proteinaceous biomass feeds are heterocycles like indoles, pyroles and pyridines and aliphatic nitrogen containing compounds like amines and amides [49].

The sulfur content of the liquefied oils (0.5-1.3 wt%) from the catalytic experiments are on average higher than the feeds (0.6 wt%), whereas those for the liquefaction experiments without catalyst addition are lower (0.1 - 0.3 wt%). This suggests that the

added sulfur for catalyst activation can serve as a reactant to form organic sulfur compounds.

The higher heating value of the liquefied-oils (33.9-36.8 MJ/kg) obtained from the catalytic liquefaction experiments are much higher than those for the oils obtained without catalysts (29.1-31.9 MJ/kg). The HHV are also higher than the HHV of the bio-oils (23.7-30.9 MJ/kg) obtained from fast pyrolysis experiments with DOSC [50], though significantly lower than petroleum products (44 - 47 MJ/kg). The energy recovery (eq. 10), increased from 67% for experiments in the absence of a catalyst to 89% in the presence of catalyst.

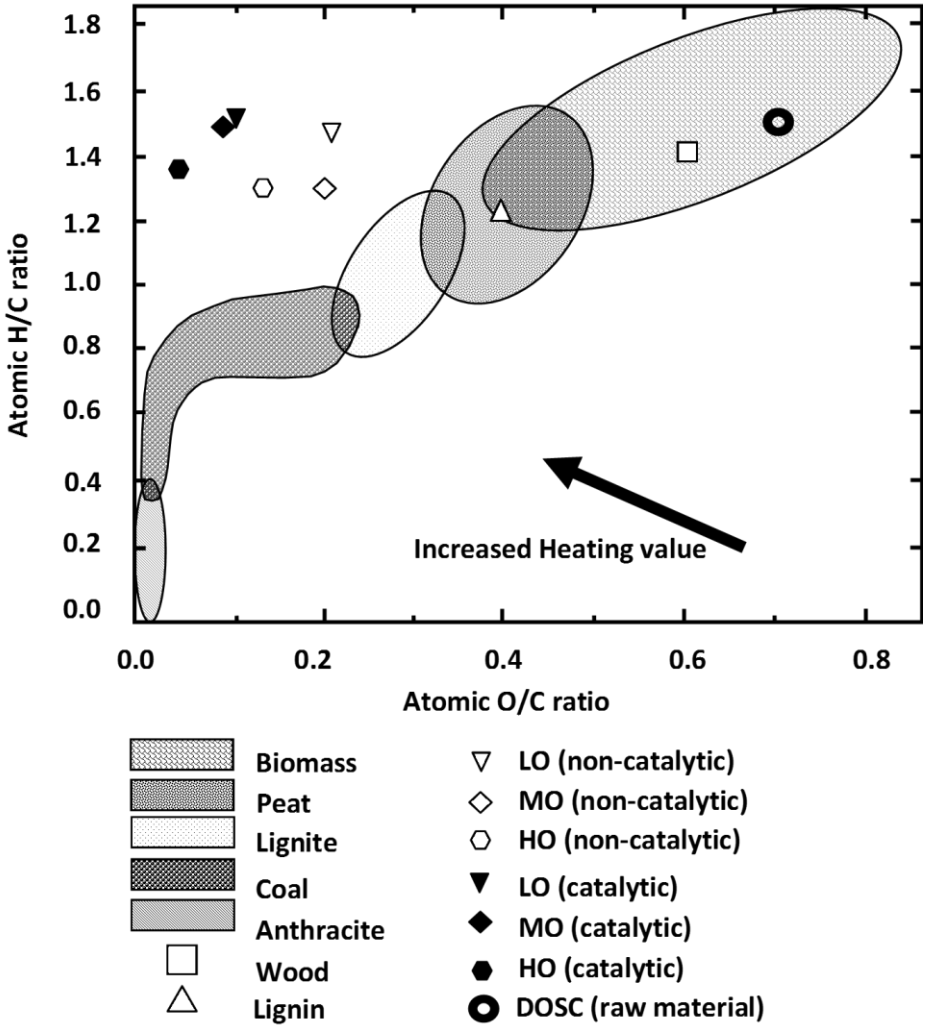


Figure 6. Van Krevelen diagram for the product oils using ethanol as the solvent

3.3.5. GC-MS analysis of liquefied oils

GC-MS has been applied to gain insights in the molecular composition of the liquefied oils [51,52]. The various fractions are multi-component mixtures, as clearly illustrated by a GC-MS spectrum for a selected LO fraction produced using ethanol as solvent with catalyst in Fig. 7. The main components were classified in four categories

being (substituted)-phenolics, nitrogen compounds, esters, and sulfur compounds (Table 4).

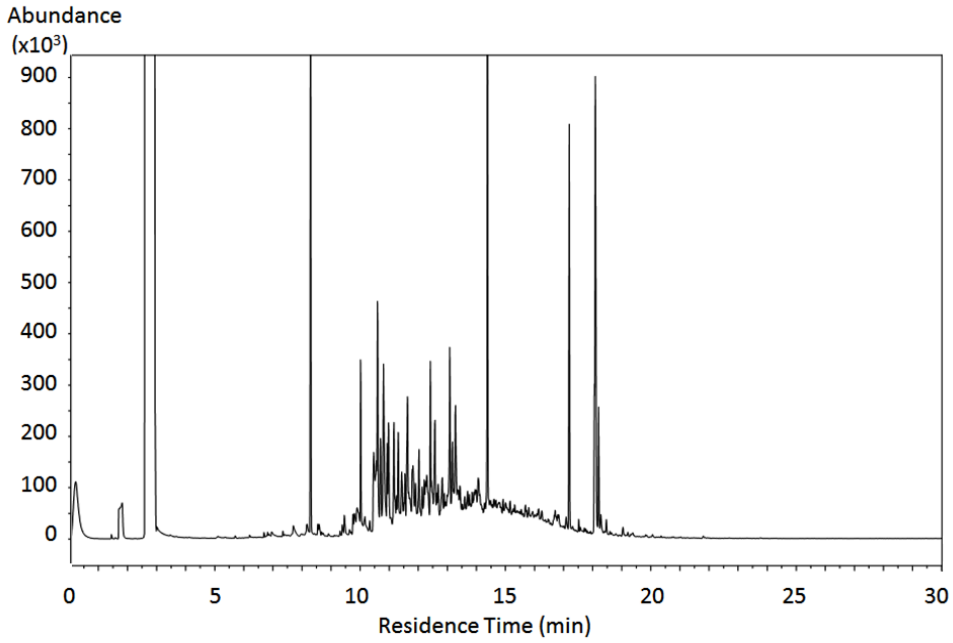


Figure 7. GC-MS spectrum of a representative LO fraction

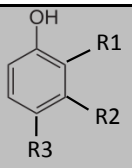
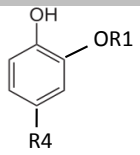
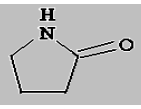
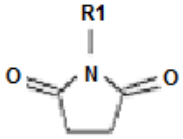
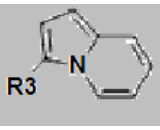
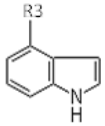
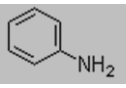
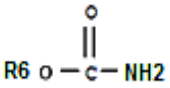
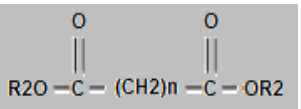
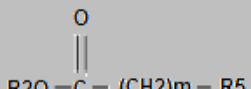
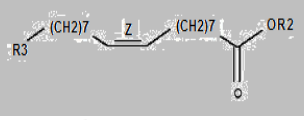
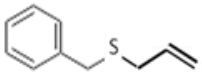
The major component groups detected in all oil fractions are esters followed by phenolic compounds and nitrogen compounds, while only one sulfur containing compound was detected in the MO fraction (3-(benzylthio)propene) .

The major individual compound in the liquefied oils is ethyl oleate (9-octadecenoic acid ethyl ester) followed by ethyl palmitate (hexadecanoic acid ethyl ester) which were found in all oil fractions. These are likely formed by a *trans*-esterification reaction of residual plant oil in the DOSC with ethanol. Some of the smaller esters may be produced by either the decomposition of the larger esters or by the formation of organic acids from subsequent reactions of carbohydrate monomer followed by an *insitu* esterification [53].

The phenolic compounds as well as guaiacols and catechols might be derived from the thermal decomposition of the lignin fraction [54]. The nitrogen compounds such as indoles, indolizines, pyrrolidones, pyrrolidinediones, aniline, and carbamatas are most likely derived from (thermal) decomposition of the proteins in the DOSC. It is well known in the literature that indoles are present in the product oils from the liquefaction of proteinaceous biomass [31,54,55].

From these results, it can be concluded that the oxygenated compounds are more concentrated in the lighter fractions (LO and MO) than the heavier fraction (HO), in line with the elemental compositions as given in Table 3.

Table 4. GC-MS data for liquefied oils

Class	Detected compounds	LO[a]	MO[a]	HO[a]	General structure[b]
Phenolics	Phenol	0.46	0.77	0.31	
	4-methyl phenol	-	-	0.36	
	2-methyl phenol	-	0.39	-	
	2-ethyl phenol	-	-	0.11	
	3-ethyl phenol	-	-	0.32	
Guaiacols and Catechols	2-methoxy phenol	1.21	1.14	0.17	
	2-ethoxy phenol	0.34	0.29	-	
	4-ethyl, 2-methoxy phenol	0.50	0.48	-	
	4-propyl, 2-methoxy phenol	0.54	0.45	-	
Pyrrolidones	2-Pyrrolidinone	0.91	2.10	0.72	
Pyrrolidinedi-ones	1-methyl, 2,5-pyrrolidinedione	0.45	0.43	-	
	1-ethyl, 2,5-pyrrolidinedione	0.89	0.81	0.08	
Indolizines	Indolizine	-	-	0.16	
	3-methyl, Indolizine	0.07	0.09	-	
Indoles	4-methyl, 1H-Indole	-	-	0.15	
	1-ethyl, 1H-Indole	-	0.07	-	
Anilines	Aniline	0.14	-	-	
Carbamates	Carbamic acid, phenyl ester	-	0.78	-	
Esters	Butanedioic acid diethyl ester	0.18	-	-	
	Pentanedioic acid diethyl ester	0.73	0.51	0.11	
	Benzenepropanoic acid ethyl ester	1.04	0.62	0.17	
	Hexadecanoic acid ethyl ester	2.49	1.97	1.50	
	Octadecanoic acid ethyl ester	0.65	0.71	0.58	
	Benzeneacetic acid ethyl ester	0.19	-	-	
	9-octadecanoic acid ethyl ester	4.19	4.70	4.49	
Benzylthio	3-(Benzylthio)propene	-	0.08	-	
TOTAL		14.98	16.39	9.23	

[a] Area percentage of total area

[b] R1=methyl/ethyl; R2=ethyl; R3=methyl; R4=ethyl/propyl; R5=Methyl/Phenyl; R6=Phenyl; n=2/3; and m =1/2/14/16

3.3.6. GPC analysis of liquefied oils

The molecular weight distributions of the product oils made in ethanol were determined using GPC and the results are shown in Fig. 8. The mass average molecular weight (M_w), number average molecular weight (M_n) and polydispersities (M_w/M_n) are presented in Table 5. The product oils produced from catalytic liquefaction experiments have a considerable lower molecular weight than the uncatalyzed ones, as is clearly visible by the reduced fraction of higher molecular weight material in Figure 8. Thus, the Fe catalyst is not only an active hydrodeoxygenation catalyst, leading to higher H/C ratio's in the product oils but also shows considerable (hydro-) cracking activity leading to a reduction in the molecular weight. The average M_w values are in agreement with those reported by Meier, *et. al.* (1986) for liquefied oils from different biomass feeds, with M_w values between 230 and 540 Dalton [56].

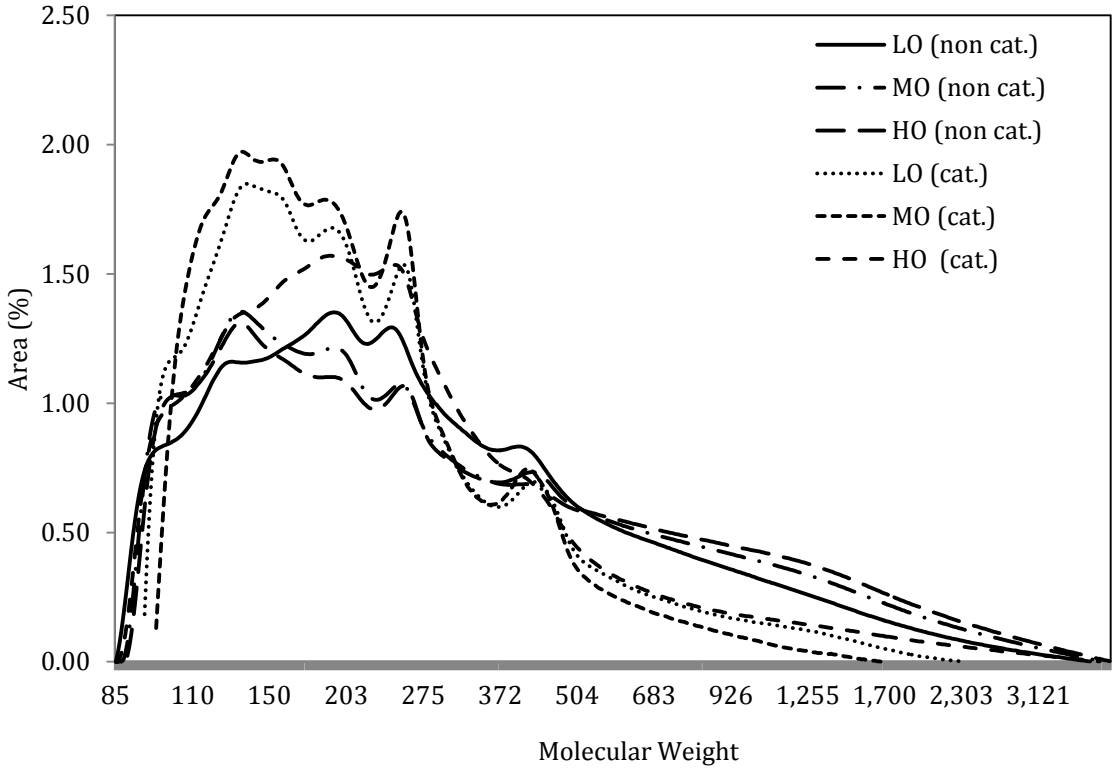


Figure 8. M_w curves of DOSC liquefied oils using ethanol as the solvent

Table 5. GPC data of product oils for liquefaction experiments in ethanol

Sample	Non-catalytic			Catalytic (Fe-limonite)		
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
Light Organic	410	227	1.81	243	186	1.31
Medium Organic	436	217	2.01	273	188	1.45
Heavy Organic	476	226	2.11	323	195	1.66

3.3.7. ^{1}H NMR analysis of liquefied oils

More information regarding the functional chemical groups present in the oils was obtained by ^{1}H NMR measurements (Fig. 9). Here, the regions in ^{1}H NMR spectra are assigned to certain functional groups and the relative amount is calculated from the peak integrals, as reported by Mullen*, et. al.* (2009) [57]. The integrated peak areas in specific chemical shift ranges are summarized in Table 6.

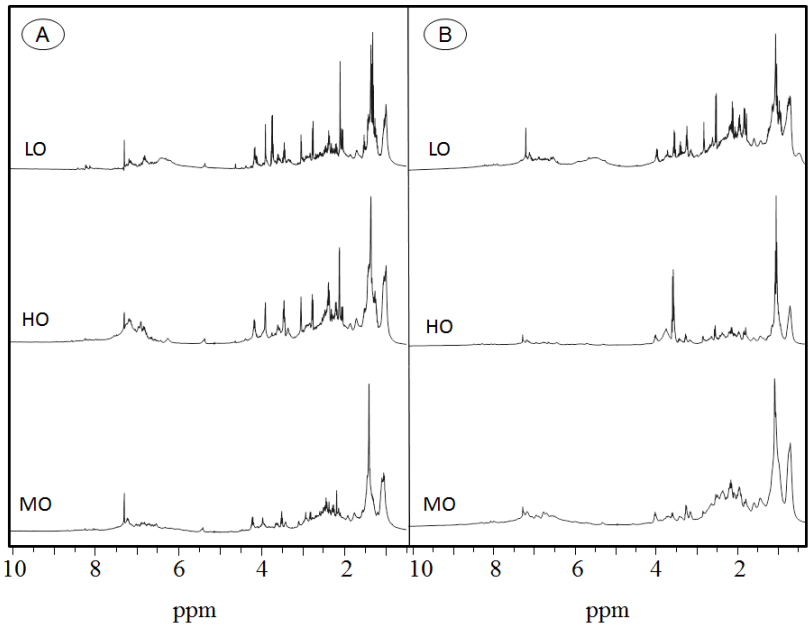


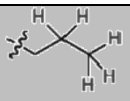
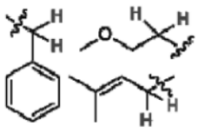
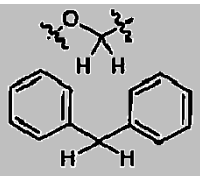
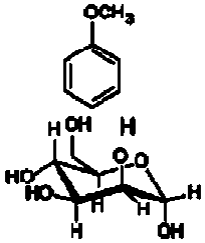
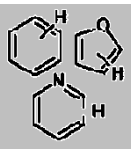
Figure 9. ^{1}H NMR analysis of product oils using ethanol as the solvent:; (A) without catalyst, (B) with Fe catalyst

^{1}H NMR spectra of the product oils show clear differences in the H-distribution in the various chemical shift ranges. All oils show high intensity peaks at δ 0.5-1.5 ppm, corresponding to alkane groups with at least two aliphatic carbons. The peak areas of the aromatic region are lower than the aliphatic one. The aliphatic/aromatic peak area ratios are between 1.3 and 8.8 (without catalyst) and between 4.3 and 6.1 (with catalyst). This indicates that the liquefied oils are considerable more aliphatic than aromatic in nature. This is consistent with the elemental composition and particularly the H/C ratio, with products having a higher H/C ratio being richer in aliphatic components. These findings are also in line with data provided by Taner, *et. al*. (2004) for the liquefaction of cotton stalk, cellulose and paper plant solid waste in aqueous acetic acid or sodium hydroxide (inert gas, 5-10 MPa and temperature 300-350°C) [52]. Here, aliphatics were found to be the main components in the product oil.

For both the catalytic and non-catalytic experiments, clear differences are observed in the aliphatic/aromatic ratio for the various product oils. The ratio is higher for the LO's and reduces in the order LO > MO > HO, indicating that the lighter oil

fractions are more aliphatic in nature. This is also supported by the elemental compositions of the oils, the LO's have a higher H/C ratio than the heavier oils.

Table 6. Functional group analysis of the product oils using ^{1}H NMR

Chemical shift region (ppm)	Type of protons	Without Catalyst			With catalyst		
		LO	MO	HO	LO	MO	HO
0.5-1.5	 Alkanes	35.19	32.46	27.53	27.46	23.21	27.13
1.5-3.0	 Aliphatics-α to Heteroatom or Unsaturation	32.36	32.56	27.35	23.89	28.22	28.54
3.0-4.4	 Alcohols, Methylene-dibenzene	13.30	12.39	12.22	18.81	14.37	11.65
4.4-6.0	 Methoxy, Carbohydrates	4.98	4.40	6.83	8.30	10.90	7.86
6.0-8.5	 (Hetero-) aromatics	12.97	15.78	18.71	15.14	16.92	18.26
9.5-10.1	 Aldehydes	0.62	1.05	2.71	2.13	2.15	2.20
	Aliphatic/aromatic[a]	8.75	5.90	1.31	6.10	5.26	4.27
	H/C[b]	1.48	1.30	1.30	1.53	1.47	1.36

[a]Ratio of the area % at 2.2-0 ppm and 8-6.4 ppm [58]

[b]Ratio of H/C, calculated from ultimate analysis

NMR data also clearly confirm the presence of nitrogen containing compounds with resonances between δ 8.5-6.0 ppm (heteroatomic or heteroaromatic containing N) and δ 4.4-3.0 ppm δ 3.0-1.5 ppm (proton resonance of methyl groups next to nitrogen) [8].

3.4. Conclusions

JCL seed cake was liquefied in the presence of four different solvents, either in the presence or absence of catalysts. The seed cake conversion and product oil yield is a function of the solvent and type of catalyst. The presence of a catalyst in DOSC liquefaction shows a positive effect on the depolymerization rate of the biopolymers in DOSC and higher oil yields were obtained. Ethanol together with limonite-sulfur catalyst resulted in the highest conversion rate and oil yield (46 wt%). Product analysis shows that the oils have a considerably higher H/C ratio than the feed. The liquefied oil of JCL seed cake is likely more suitable for use as a chemical feedstock than as a fuel due to the relatively high amounts of nitrogen. Extraction studies to isolate and concentrate valuable organic nitrogen containing molecules are in progress.

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Chapter 4

Valorization of *Jatropha curcas* L. Seed Cake using Fast Pyrolysis Technology

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Abstract

The pyrolysis of *Jatropha curcas* L. (JCL) seed cake was investigated in a continuous bench scale pyrolyzer using rotating cone fast pyrolysis technology at a scale of about 2.5 kg/h. The pyrolysis oil yield and relevant physical and chemical characteristics (acidity, elemental composition, molecular weight distribution, GC-MS, 2D-GC) were determined. Spontaneous phase separation of the pyrolysis liquids was observed after pyrolysis to an apolar organic and a polar aqueous phase. The total liquids yield was between 50 and 55 wt% (dry ash free basis, daf) at pyrolysis temperatures in the range 479-507°C, the remainder being char (19-21 wt% daf) and gas (16-16 wt% daf). The pyrolysis oils contain relatively large amounts of nitrogen and oxygen, and a small amount of sulfur. The major constituents are organic acids, phenolics and N containing compounds, the major being acetic acid, 2-furanmethanol, butyrolactone and 2(5H)-furanone.

4.1. Introduction

Important global issues related to the use of fossil resources (security of supply, environmental problems) have encouraged many researchers to search for alternative, CO_2 neutral energy sources. Biomass is one of the promising alternatives due to its wide spread availability and renewability. In addition, biomass production can generate income and employment in developed and developing countries. Moreover, if appropriate crops are selected, restoration of degraded lands may also be possible [1]. Preferentially, the biomass type is selected in such a way that it does not directly compete with food products. An example of such a crop is *Jatropha curcas* L. (JCL), a small tree that produces seeds with high oil content suitable for biodiesel production. The oil is non-edible and as such does not directly compete with food applications.

The *Jatropha* shrub is promoted as a multipurpose plant with many attributes and considerable potential. It can be grown in low to high rainfall areas and can be used to reclaim land, as a hedge and/or as a commercial crop [2]. Therefore, it is also beneficial for land conservation. Unfortunately, up to now the commercialization of JCL to produce biodiesel has faced many economical and technical issues. One of the possibilities to improve the economical feasibility is by applying the biorefinery concept. In this concept, the focus is not solely on one single product like the oil but aims for full valorization of all by- and waste products into value-added products, while minimizing the loss of energy and mass, and as such maximize the overall value of the production chain [3].

Upon processing the seeds to oil, a seed press cake is obtained as a byproduct. To increase the economic potential, valorization of the JCL seed cake and seed shells are of high importance. The JCL press cake has potential to be used for biogas production [4], as an organic fertilizer [5] for animal feed [6], for enzyme production [7] and for binderless board manufacture [8]. Another interesting conversion technology for the seed cake is fast pyrolysis. However, to the best of our knowledge, fast pyrolysis technology has not been demonstrated on kilogram scale for JCL seed cake valorization.

Fast pyrolysis of biomass involves heating the biomass rapidly in an inert atmosphere to temperature between 450-550°C [9]. Oil yields up to 70 wt% may be obtained. At higher temperatures and longer residence times, more gas and less solid residues are produced [10]. The utilization of various seed cakes for pyrolysis processes have been reported. Examples are safflower [11] [12], cotton [13] [14], rapeseed [15] [16], polanga [17], pennycress and camelina seed cake [18]. Typical pyrolysis oil yields are between 14 and 60% and depend on feedstock type, heating rate and temperature, particle size, swept gas flow rate, reactor type and the presence of catalysts. The elemental composition of the pyrolysis oils on dry basis ranges from 61.8 to 73.7% carbon, 6.3 to 10.7% hydrogen, 3.8 to 9.1% nitrogen and 10.5 to 27.2% oxygen, giving atomic H/C and O/C in the range 1.13-1.74 and 0.11-0.33, respectively. Higher heating values (HHV) were reported to be between 23 and 50 MJ/kg. In addition, some research has also been performed on seed cakes pyrolysis involving a catalyst (catalytic

pyrolysis) [19] and in a hydrogen environment (hydropyrolysis) [20]. The use of a catalyst was shown to have beneficial effects for the pyrolysis of cotton seed cake and particularly on the product properties of the pyrolysis oil in terms of calorific value, hydrocarbon distribution and removal of oxygenated groups.

Biomass pyrolysis involves very complex reaction pathways, consisting of many serial and parallel reactions [21]. These reactions are not only affected by the operating conditions but also by the composition and morphology of main biomass constituents (cellulose, hemicellulose and lignin) [22]. Moreover, seed cakes contain substantial amounts of protein, which show different reactivities than those mentioned above. The presence of inorganic matter (mineral) in biomass is a further complication as it may catalyze various reactions and as such affect product yields and composition [23].

The main objective of the present study is to investigate the valorization of JCL seed cake by fast pyrolysis using rotating cone technology developed by BTG (Biomass Technology Group, Enschede, the Netherlands). This technology has been demonstrated successfully on a 2 ton/h scale [24]. The experiments were conducted in a down-scaled continuous reactor on a scale of several kg/h, and as such that the data are representative for larger scale operation. Relevant product properties and the chemical composition of the pyrolysis oils are reported and compared with other reference pyrolysis oils. This includes chromatographic and spectroscopic techniques such as GPC, GC-MS and 2D-GC, elemental analysis, and other physico-chemical analysis.

4.2. Experimental section

4.2.1. Materials

JCL seed cake (SC) was produced at an expeller processing unit at B2TE – BPPT Indonesia using dehulled seeds and stored at 4°C before further processing to inhibit the growth of microorganisms. The JCL SC was crushed to particle sizes < 1 mm using a hammer mill equipped with a perforated steel plate with 1 mm holes. The crushed SC was processed further in a continuous extraction unit at Germany (Pilot Pflanzenöltechnologie Magdeburg e.V.) using hexane to remove residual oil. The de-oiled seed cake (DOSC) produced was used as raw material in the pyrolysis experiments. The DOSC was dried to a moisture content of about 9 wt% using an electrical oven at 105°C before use.

4.2.2. Analytical methods

4.2.2.1. Proximate analysis of DOSC

The proximate analysis of DOSC was performed using a LECO TGA 501 thermogravimetric analyzer. The moisture content determination of DOSC was

performed according to ASTM E871 - 82(2006), ash content using ASTM D1102 - 84(2007), and volatile matter content using ASTM E872 - 82(2006).

4.2.2.2. Elemental composition and heating value of DOSC and pyrolysis products

The elemental composition of the DOSC and the pyrolysis oils (C, H, N and S) were determined using a Euro Vector 3400 CHNS analyzer, while the oxygen content was determined by difference. The reported values are the average of two independent analysis. The higher heating value (HHV) of the oils was calculated using the Channiwala (2002) equation (Eq. 1) where C, H, S, O, N and A represents carbon, hydrogen, sulfur, oxygen, nitrogen and the ash content in mass percentages on dry basis [25].

$$HHV\ (dry) = 0.3491C + 1.1783\ H + 0.1005\ S - 0.1034\ O - 0.0151\ N - 0.0211\ A \quad (MJ/kg)$$

4.2.2.3. Water content of product oils

The water content of the pyrolysis oils was determined by Karl Fischer titration using an Metrohm Titrino 758 titration device. A small amount of the oil sample (0.03 – 0.10 g) was added to an isolated glass chamber containing hydranal (Karl Fisher solvent, Riedel de Haen). The titrations were carried out using the Karl Fischer titrant composit 5K (Riedel de Haen). All measurement were conducted in duplo.

4.2.2.4. 2D-GC and GC-MS-FID analysis

2D-GC analysis were performed on a trace 2D-GC from Interscience equipped with a cryogenic trap system and two columns, a 30 m x 0.25 mm i.d. and a solgel capillary column (0.25 µm film thickness) connected to a 148 cm x 0.1 mm i.d. and a Restek 1701 column (0.1 µm film thickness). An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the coldtrap is 60 °C. Helium was used as the carrier gas (flow 0.6 ml/min). The injector temperature and FID temperature were set at 250 °C. The oven temperature was kept at 60 °C for 5 minutes then heated up to 250 °C at a rate of 3 °C min^{-1}. The pressure was set at 0.7 bar. The modulation time was 6 s.

GC-MS-FID analysis were performed on a Hewlett Packard 5890 series II plus with a Quadrupole Hewlett Packard 5972 MSD and an FID. The GC was equipped with a 60 x 0.25 mm i.d. and Restek RTX-1701 capillary column (0.25 mm film thickness). The exit stream was split in a 1:1 ratio and fed to an MSD and FID. The injector temperature was set at 250 °C. The oven temperature was kept at 45 °C 318 K for 4 minutes then heated up to 275 °C at a rate of 4 °C min^{-1}.

The concentrations of individual compounds were obtained by considering the relative response factor (RRF). For the RRF of individual compounds which were not used as calibration standards, an average RRF for the component class was used. This value was obtained by experimental determination of at least two RRF values of model compounds representative for the component class [26]. Model compounds were injected 3-4 times with different levels of dilutions. DBE (di-n-butyl ether) in THF was used as the internal standard. For all compounds, the probability according to the MS library was higher than 80% and for most higher than 90%.

A gas meter type G6RF1 from *Itron* was used to measure the gas volume flow rate, while the concentrations of H_2, O_2, N_2, CH_4, CO, CO_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8 were determined with an online *Synspec* gas chromatograph (GC type 955).

4.2.2.5. GPC analysis

The molecular weights and molecular weight distributions of the samples were determined by gel permeation chromatography (GPC) with a system consisting of a Model Hewlett Packard 1050 pump, a Model 410 differential refractometer and three thermostated (35 °C) Shodex KF series columns. THF was used as the mobile phase. The flow rate was set at 0.55 mL/min and the pressure at 140 bars. The columns were calibrated with polystyrene standards of known molecular weight and narrow molecular weight distribution. The column was operated at 40°C. The injection volume was 25 µl with a sample concentration of 1.0 g/L. The analysis for a sample was complete within 30 min.

4.2.2.6. Viscosity measurements

The viscosity of the samples was measured using a cone and plate rheometer (TA instruments, AR-1000-N) at 22.4 °C and a fixed shear rate valueof 1.67 s^{-1}.

4.2.2.7. pH measurements

The pH of each sample was measured using a 691 pH meter from Metrohm. The sample was added to water in a 1:1 volume ratio and mixed thoroughly. Then the water fraction was separated and the pH was determined.

4.2.2.8. TGA measurements

A Perkin Elmer-TGA7 equipped with Pyris software was used to determine the thermal behavior of a sample. Approximately 20 mg of DOSC sample was used and spectra were recorded between room temperature and 900 at a 10°C /min heating rate. Oxygen was used as the purge gas at a flow rate of 20 ml/min. For pyrolysis oils, approximately 10 mg of sample was heated from room temperature to 900°C at a constant 10°C/min heating rate under N_2 gas with a flow rate of 20 ml/min.

4.2.2.9. Fast pyrolysis experiments

The fast pyrolysis experiments were carried out in a continuous fast pyrolysis unit with a maximum throughput of 5 kg/h using rotating cone technology schematically presented in Figure 1 [3]. The pyrolysis experiments were performed at atmospheric pressure and three temperatures using a run time of about 2.5 h per run. The process conditions for each experiment are summarized in Table 1.

The feeding system of the pyrolysis unit was calibrated using the dried DOSC to pre-determine the input feed rate. During these calibration tests, the DOSC was processed through the feeding section, which resulted in a particle size reduction of the DOSC.

In a typical experiment, DOSC was fed into the pyrolyzer through a screw conveyor with a feeding rate between 2.3 and 2.5 kg/h. The pyrolysis vapors were liquefied in two successive condensers (1 and 2) at temperatures of around 40°C (Figure 1). Cooling was performed by spraying the vapors with cold fast pyrolysis oil. At the start-up of the process, both condensers were partly filled with start-up oil, in this case fresh pine wood pyrolysis oil. During the experiments, various oil fractions were collected in both condensers. The oils from the condensers were tapped periodically and collected. The product oils phase separated upon standing into an aqueous fraction (water phase) and a viscous fraction (organic phase). The fractions were separated, analyzed and weighed for mass balance calculations. Product yields are the combined yields of both condensers after reaction.

Product #5 from condenser 1 (both the organic and aqueous fractions) obtained at a pyrolysis temperature of 507°C was selected for detailed physical and chemical analysis as it was considered the most representative product sample.

The total char yield is the sum of the amount of char combusted within the system and the amount of char recovered from the cyclones. The amount of char combusted is measured indirectly using the oxygen balance over the combustor. The amount of oxygen required for combustion is the difference between the oxygen entering the combustor and the oxygen leaving in the flue gas. The oxygen in air entering the combustor is measured before the experiment. The volume flow and oxygen content in the flue gas are measured at several intervals during the experiments to determine the amount of oxygen leaving the combustor. The amount of char obtained from the cyclones is obtained by collecting the total amount of solid material in the cyclones after a run. These solid samples contain ash, sand and char. The amount char in this sample is determined by heating up a sample of the material to 550°C under oxidative conditions for 4 h. The relative weight loss is the relative char amount in the total solid sample. The remainder is ash and sand. In the overall balance, the amount of sand in the ash is fitted in order to obtain a 100% ash balance closure.

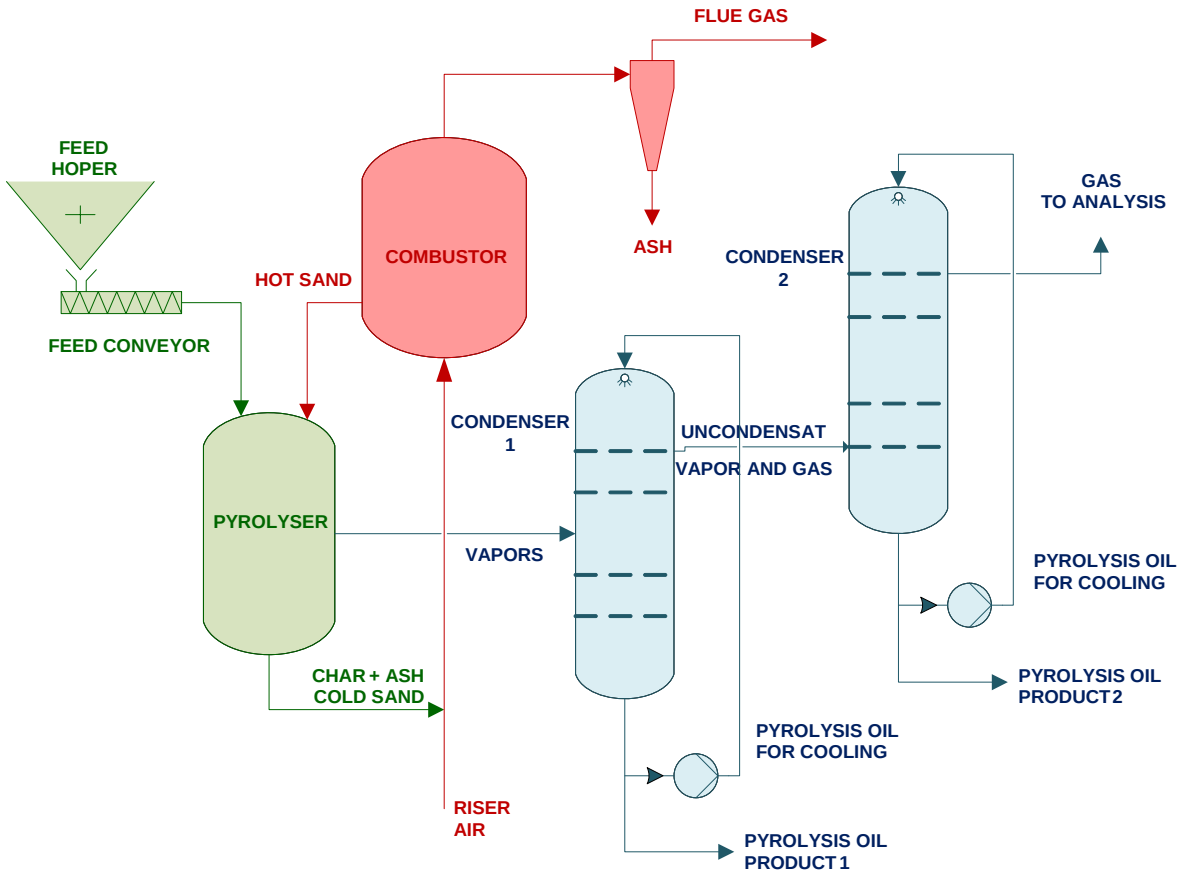

Figure 1. Schematic diagram of the pyrolysis experimental setup used

Table 1. Input parameter of the pyrolysis experiments

	Run No.		
	1	2	3
Combustor (T, °C)	565	588	626
Sand (reactor in) (T, °C)	509	526	544
Sand (reactor out) (T, °C)	449	456	470
Pyrolysis (average) (T, °C)	479	491	507
Feed rate (kg/h)	2.3	2.5	2.3
Moisture content DOSC (wt%)	9.0	9.3	9.0

The pyrolysis experiments were conducted at three pre-set combustor temperatures in the range 565 – 626°C. The actual reactor sand inlet temperatures were between 509 and 544°C and the corresponding outlet temperatures between 449 and 470°C. For each experiment, the reactor is assumed to be operated at the average temperature of the sand in and outlet and this value is taken as the reference pyrolysis temperature for an experiment (Table 1).

4.3. Results and discussions

4.3.1. Chemical and physical properties of the Jatropha seed cake

The JCL de-oiled seed cake (DOSC) mainly consists of polysaccharides (cellulose and hemicellulose, 33 wt%), proteins (28 wt%) and lignin (29 wt%) [8]. An overview of the relevant characteristics of the DOSC is given in Table 2. Of particular relevance for the pyrolysis research described here is the ash content of 8.57 wt%, mostly in the form of minerals such as potassium, calcium, and magnesium [27].

The major elements found in DOSC are C, H, O and N (Table 2) with values of 45.16, 5.76, 41.42 and 7.39 % (daf) respectively, and small amounts of sulfur (0.27%). The nitrogen content is relatively high due to the presence of considerable amounts of proteins in the kernel.

Table 2. Characteristics of DOSC

Analysis	Component	Value (wt%)
Proximate[a]	Moisture	10.25
	Volatile Matter	47.95
	Fixed Carbon	36.69
	Ash	8.57
Ultimate[b]	Carbon	45.16
	Hydrogen	5.76
	Nitrogen	7.39
	Oxygen (by diff.)	41.42
	Sulfur	0.27
Calorific value[a]	HHV (MJ/kg)	14.15
Empirical formula[b]	$CH_{1.53}N_{0.14}O_{0.69}S_{0.023}$	

[a] as received basis; [b] dry ash-free basis

The thermal gravimetric and differential thermal analysis of the DOSC is given in Figure 2 and shows the typical characteristic of a lignocellulosic material. The first mass loss peak (< 180°C) represents evaporation of moisture and extractives from the DOSC. The DOSC started to decompose at 200°C, and almost quantitative decomposition was observed at 620°C. The maximum weight loss peak at about 300°C is due to degradation of the hemicellulose and cellulose fraction [8]. A clear DTG peak of lignin is not observed, which is in line with literature data indicating a broad temperature peak for lignin degradation. At 500°C, the weight loss was about 70 wt%. Thus, a pyrolysis temperature of about 500°C seems appropriate for subsequent larger scale pyrolysis experiments.

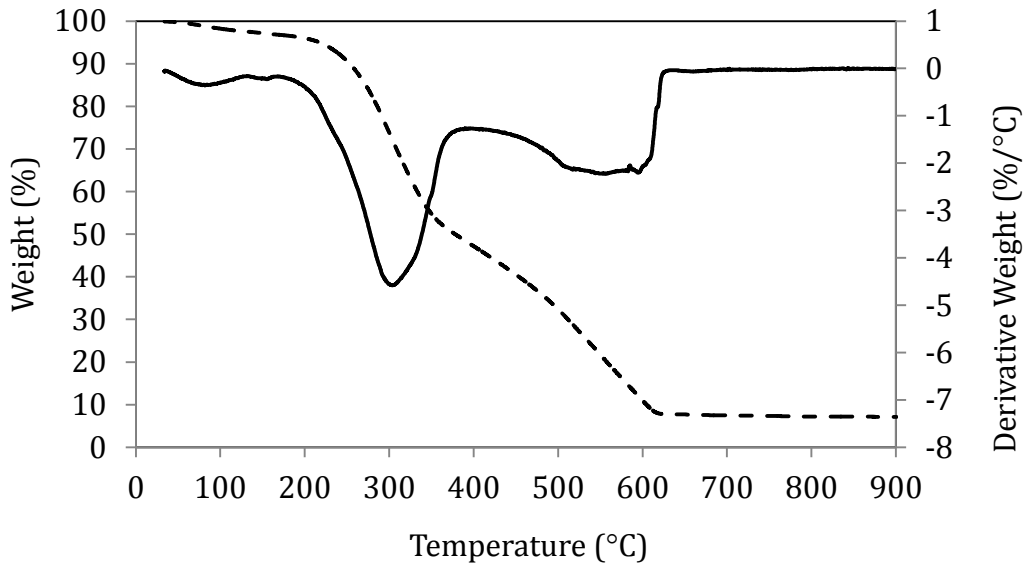

Figure 2. TG and DTG curve of JCL DOSC

4.3.2. Pyrolysis experiments

The fast pyrolysis experiments of the DOSC were carried out in a continuous flash pyrolyzer with a throughput between 2.3-2.5 kg/h using rotating cone technology (Figure 1). The DOSC was dried to a water content of about 9 wt% before use (Table 1). The product yields and mass balance are provided in Table 3. The liquids collected from condenser 1 consisted of two layers: an aqueous phase upper layer and a dark brown viscous layer with a density higher than water. Apparently, the product oil spontaneously phase separates after formation. This phenomenon has been observed before in the literature for pyrolysis experiments using seed cakes [12] [28]. In the following, the aqueous top phase will be designated as the aqueous fraction and the dark brown bottom layer as the organic fraction.

Table 3. Mass balance for the fast pyrolysis process of JCL seed cake

Product	Yield of products (wt% daf)		
	479°C	**491°C**	**507°C**
Total liquid [a]	50	52	57
- Total organics[b]	29	29	34
- Water[b]	21	23	23
Gas	16	16	18
Char	21	19	21
Total	87	87	96

[a] Sum of the aqueous and organic phase [b] total organics is total amount of organics in both liquid phases and is calculated from the yield of the organic and aqueous phase in combination with known water content. Calculation is on a daf basis.

Mass balance closure of the experiments was satisfactorily and between 87% and 96%. The main issue was the determination of the char content, which was determined indirectly (see experimental section). The total liquid yields were in the range of 50-57 wt% daf (Table 3). These yields are at the high end of the range reported for seed cake pyrolysis (14-59 wt%), though comparison is cumbersome as different work-up protocols for the oils were applied (e.g. solvent extraction).

It is not possible to draw sound conclusions regarding the effect of the pyrolysis temperature on the product yields due to the narrow temperature range studied in combination with the less than quantitative mass balance closures.

4.3.3. Properties and elemental composition of the liquid phases

4.3.3.1. Elemental composition of the liquid phases

In Table 4, the elemental composition of the pyrolysis oil fractions (organic and aqueous phase) are provided and compared with pyrolysis-oils from other seed cakes. The analysis were performed for the organic and aqueous fractions of the experiment at 507°C and particularly the fifth batch collected in condenser 1. This sample is considered the most representative as start-up effects are eliminated. Both phases contain significant amounts of water, *viz.* 17.15 wt% for the organic phase and 61.75 wt% for the aqueous phase.

Table 4. Comparison of relevant yields and elemental composition of pyrolysis oils from different seed cakes

Parameter	Safflower seed cake[a] [11] [12]	Cotton seed cake[b] [13] [14]	Rape seed cake[b] [16] [15]	Soybean cake[c] (29)	Sunflower[a] [30] [31]	DOSC (this study)	
						Organic Fraction[a]	Aqueous fraction[a]
C (wt%)	61.78-67.59	65.0-69.57	64.05-73.74	67.17	63.7-68.5	70.63	53.04
H (wt%)	6.29-8.21	8.4-9.36	8.48-10.69	9	8.2-9.9	6.66	6.05
O (wt%)	20.05-27.23	15.95-20.8	10.51-18.37	13.06	16.0-19.8	14.23	30.02
N (wt%)	3.29-4.92	5.68-6.06	4.65-9.05	10.78	4.5-8.3	8.12	10.88
S (wt%)	<0.1	-	0.11-0.59	-	-	0.36	<0.003
H/C (mol/mol)	1.13-1.56	1.52-1.64	1.56-1.74	1.6	1.54-1.73	1.12	1.68
O/C (mol/mol)	0.22-0.33	0.18-0.24	0.11-0.21	0.15	0.175	0.15	0.42
HHV(MJ/kg)	30.0-36.8	30.4-33.8	32.9-36.4		32.2	30.9	23.7

[a] Elemental analysis on dry ash free (daf) basis, [b] Elemental analysis after solvent extraction procedure, [c] two phase liquid, elemental analysis are given for the oil phase

The carbon content of the organic fraction is considerably higher than that of the aqueous fraction. However, it is clear that the aqueous fraction still contains significant amounts of polar organics as reflected by the carbon content (53 wt%). Thus, it appears that phase separation leads to an organic phase enriched in relatively apolar organics and a more polar fraction with significantly more water and large amounts of polar

organics. The weight average carbon content of both fractions is in the range of the pyrolysis liquids produced from other seed cakes (Table 4).

The DOSC organic fraction contains considerable amounts of heteroatoms such N, O and S. The N-contents are 8.12% daf (5.51% wet) and 9.23% daf (2.82 % wet) for the organic and aqueous fraction respectively. The O content of the aqueous fraction is 30.02% daf and 14.23% daf for the organic phase, and the weight average is in the typical range for pyrolysis oils from other seed cakes (Table 4).

The elemental composition of the two liquid fractions and the DOSC feed were compared in terms of the atomic H/C and O/C ratio in Van Krevelen diagram (Figure 3). The atomic ratio H/C and O/C of DOSC (1.52 and 0.72) is in the same range as for typical lignocellulosic biomass. In addition, the values are also in the range reported for typical seedcakes, though a large spread in values was observed (Figure 3). The elemental composition of the two liquid fractions after pyrolysis differs considerably, see Figure 3 for details. The O/C and H/C ratio of the aqueous fraction are higher than found for the organic fraction. This indicates that the polar organics in the aqueous phase have relatively high oxygen content compared to those in the more apolar fraction, which is to be expected based on structure-property relations. In Figure 3, also the elemental compositions of pyrolysis products from other seed cake are provided. Comparison is cumbersome as the product oils are often not isolated as such but obtained by a solvent extraction procedure which changes the elemental composition. In comparison with other pyrolysis oils of seed cakes, the organic fraction from DOSC pyrolysis shows relatively low O/C and H/C ratios (Figure 3). However, the elemental composition of the combined organic and aqueous phase is well in the range for other pyrolysis oils from seed cakes.

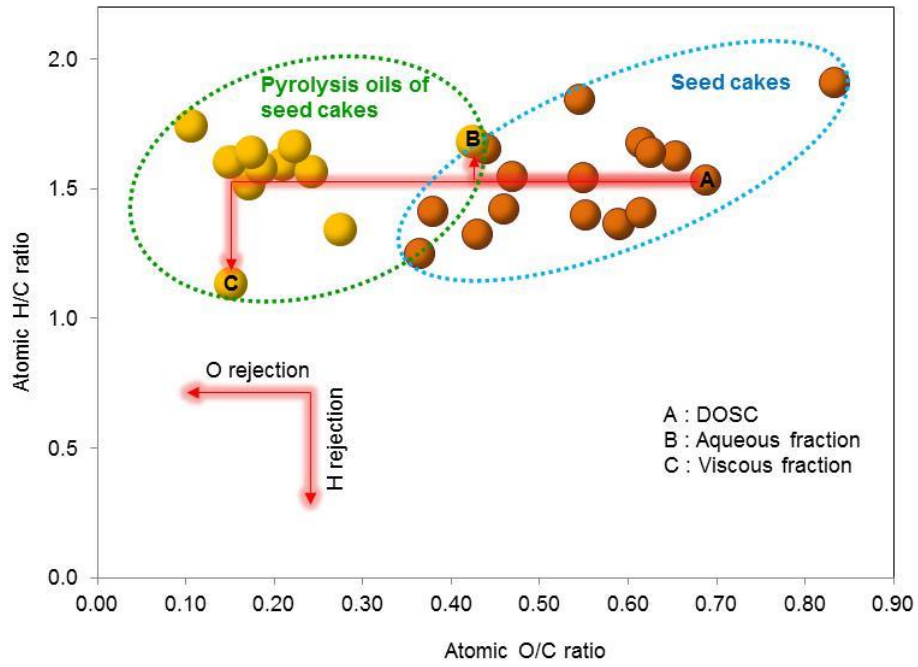

Figure 3. Van Krevelen plot for seed cakes and pyrolysis oils derived thereof by pyrolysis technology (input given in Table 4, dry basis)

4.3.3.2. Product properties

The pH value of the aqueous fraction is 5.05 (Table 5), which is indicative for the presence of organic acids. The acidity of the organic fraction could not be determined accurately due to its apolar nature. However, GC analysis indicates the presence of acetic acid in the organic fraction as well, with amounts close to those in the aqueous phase. The typical pH of pyrolysis liquids produced from wood, grasses, and other conventional lignocellulosic biomass sources has been reported in the range between 2.0 and 3.0 [32]. Thus, the acidity of the pyrolysis oils from DOSC is considerably lower than for typical biomass pyrolysis oils. This is likely due to the presence of N compounds which have basic properties and will neutralize part of the acids.

The density of the organic phase (1.14 g/ml) is considerably higher than that of the aqueous fraction (1.05 g/ml), in agreement with the phase separation behavior. The values for the organic phase are close to those obtained for the organic phases (after solvent extraction) for soybean cake and safflower cake (Table 5), though considerably higher than for rapeseed cake.

The viscosity of the organic fraction is considerably higher (80 times) than that of the aqueous fraction, due to the lower amount of water and likely the presence of higher molecular weight compounds (*vide infra*).

Table 5. Comparison the physical properties of pyrolysis oil from different seed cakes

Property	Soybean cake[a] [28]	Safflower cake[a] [11]	Rapeseed cake[b] [33]	JCL DOSC (this study)	
				Organic fraction	Aqueous fraction
pH	-	-	-	-	5.05
Viscosity (cP)	72.38	225	14.4-26.2	431	5.1
Density (g/ml)	1.11	1.08	0.96-0.98	1.14	1.05

[a] Properties of the organic phase after solvent extraction procedure; [b] two phase oil, data are given for the organic phase

4.3.3.3. Molecular composition

Multidimensional GC and GC-MS were applied to gain insights in the molecular composition of the organic and aqueous fraction. Particularly 2D-GC has proven to be very suitable to classify and semi-quantify the various component groups present in fast pyrolysis oils [8]. From the 2D-GC and GC-MS-FID results (Figure 4 and Table 6) a number of organic compound groups were identified. The groups were classified according a general classification system used in the literature for pyrolysis oils (26). The various components belonging to the same homolog groups are almost completely

separated, only some acids (fatty acids) overlap with phenolic derivatives in the 2D-GC chromatograms. Table 6 summarizes the concentrations in the fractions of the 44 main components, which were quantitatively determined by GC-MS-FID. The total concentration of identified and quantified components is by far less than 100%, indicating the presence of higher molecular weight compounds (dimers, trimers, and oligomers) that are insufficiently volatile for GC analysis [34]. This was confirmed by subsequent GPC measurements (*vide infra*).

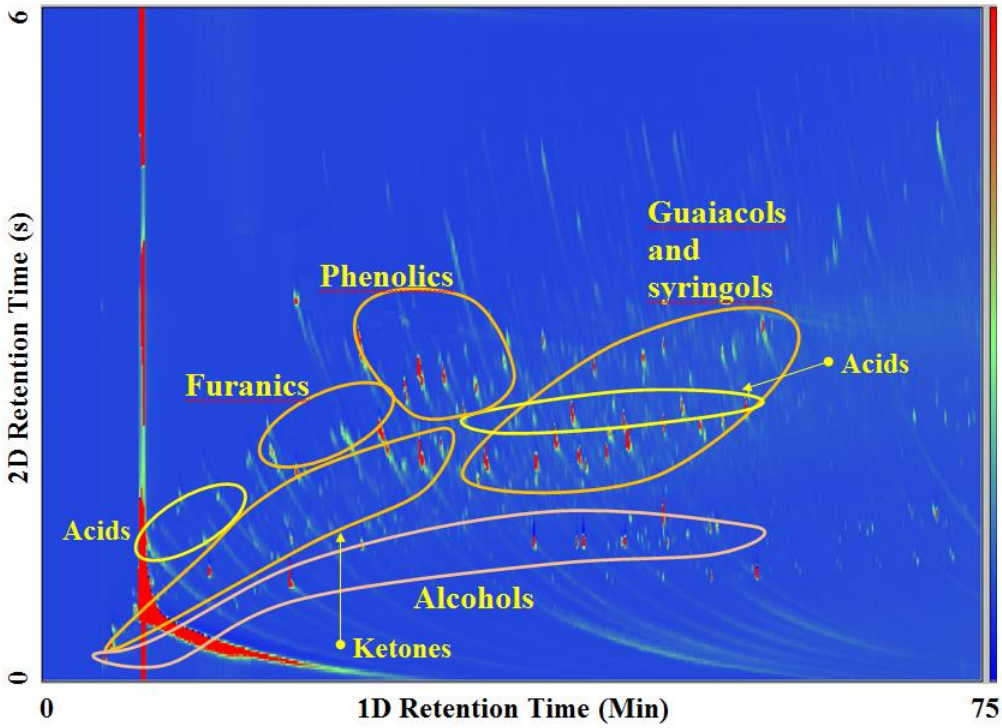

Figure 4. Typical 2D-GC chromatogram of the organic phase obtained at 507°C

Besides water, acetic acid is the most abundant molecule in both organic and aqueous fraction (0.83 and 0.71 %, respectively), which is in agreement with the results obtained for rapeseed pyrolysis [35]. The presence of higher organic acids (dodecanoic acid, heptadecanoic acid) in the organic fraction is likely the result of the thermal degradation of residual amounts of triglycerides in the DOSC

Numerous phenolic compounds were detected in the organic phase; examples are substituted methoxy phenolics like 2-methoxyphenol and eugenol. These phenolics are expected to be derived from the lignin fraction of the DOSC [36]. Almost all phenolic compounds were found in the organics fraction, and only a few in the aqueous fraction, in line with their relatively apolar nature.

Levoglucosan (1,6-anhydro-β-D-glucopyranose) was detected only in the aqueous fraction. It is known to be formed by the degradation of cellulose and the C6 fraction of hemicellulose. Other chemical compounds derived from the degradation of

cellulose and hemicellulose fraction of the DOSC are furanics, cyclopentenes, and acetol (1-hydroxy-2-propanone) [36].

Numerous N-containing compounds such as aniline, benzeneacetonitrile, 4-hydroxy-benzeneacetonitrile and acetamide were detected and are produced from the pyrolysis of the proteins in the DOSC [33]. All of these N-containing compounds were present only in the organic fraction, except for acetamide that was detected in both the organic and aqueous fraction. The total amounts of N-containing molecules detected by GC is low (0.7 wt%), when compared to the N content of the organic and aqueous fraction (8.12-10.88 wt% dry basis).

Table 6. GC-MS analysis of the organic and aqueous phase obtained from a pyrolysis experiment at 507°C

Compound	Conc. (wt%)	
	Organic phase	Aqueous phase
Acids		
Acetic acid	0.83	0.71
Propanoic acid	0.12	0.2
Octanoic Acid		0.33
Dodecanoic acid	0.32	
Heptadecanoic acid	0.19	
Ketones		
Acetone	0.34	
2-Propanone, 1-hydroxy-		0.09
2-Cyclopenten-1-one	0.08	
2-Cyclopenten-1-one, 2-methyl-	0.07	
2-Cyclopenten-1-one, 3-methyl-	0.08	
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	0.33	0.11
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.07	
4-Hydroxy-3-methylacetophenone	0.24	
FAE		
Butanoic acid, butyl ester	0.08	0.06
Guaiacols and syringols		
Phenol, 2-methoxy-	0.57	0.06
Phenol, 2-methoxy-4-methyl-	0.33	0.05
Phenol, 4-ethyl-2-methoxy-	0.33	
Phenol, 2-methoxy-4-(1-propenyl)-	0.15	
Eugenol	0.14	
Phenol, 2,6-dimethoxy-	0.24	
Phenol, 2-methoxy-4-(1-propenyl)-	0.12	
Phenol, 2-methoxy-4-(1-propenyl)-	0.52	
Vanillin	0.09	

Compound	Conc. (wt%)	
	Organic phase	**Aqueous phase**
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	0.05	
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.04	
Phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.13	
Alcohols		
Ethanol	0.16	0.19
Furanics		
2-Furan methanol	1.59	0.58
2(5H)-Furanone	0.81	0.55
Phenolics		
Phenol	0.28	0.03
Phenol, 2-methyl-	0.07	
Phenol, 4-methyl-	0.19	
Phenol, 3-methyl-	0.09	
Phenol, 2,4-dimethyl-	0.05	
Mequinol		0.08
Sugars		
1,6-Anhydro-b-D-glucopyranose		0.65
N-containing compounds		
Aniline	0.11	
Benzeneacetonitrile	0.25	
Benzeneacetonitrile, 4-hydroxy-	0.09	
Acetamide	0.24	0.08
Hydroquinones		
Hydroquinone	0.14	
Hydroquinone, methyl-	0.08	
Misc. organics		
Butyrolactone	1.32	0.88
Toluene	0.02	
TOTAL	10.96	4.65

The molecular weights of the liquid phases produced in the experiment at 507°C were analyzed by GPC in THF and the results are given in Figure 5. The molecular weight of organic fraction is considerably higher than for the aqueous fraction, this is particularly evident from the large molecular weight tail. This confirms the presence of considerably larger amounts of higher molecular weight compounds in the organic fraction.

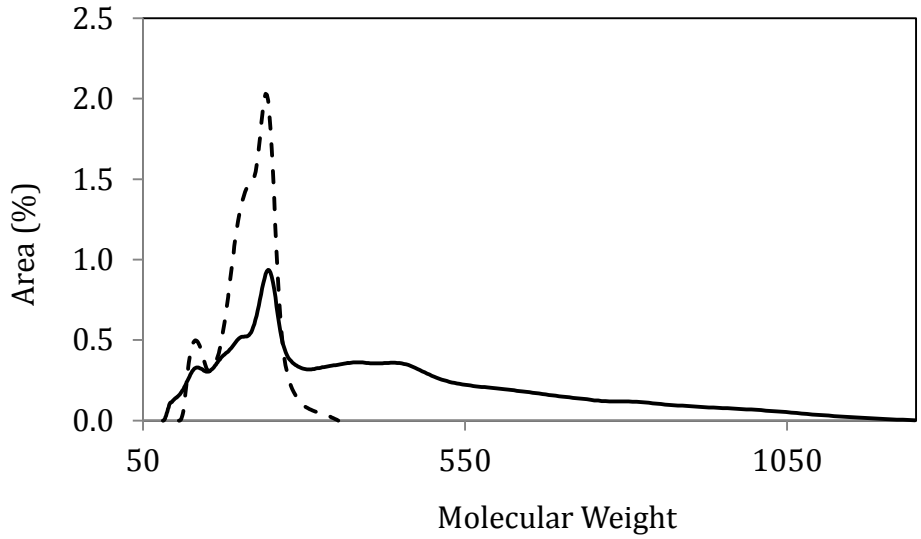

Figure 5. Molecular weight distributions by GPC for the organic (solid) and aqueous fraction (dash)

TG/DTG analysis is a useful technique to characterize the evaporation, thermal decomposition and combustion properties of pyrolysis oils [37]. Both the organic and aqueous products from an experiment at 507°C were analyzed under N_2 at a heating rate of 10°C/min. The thermogravimetry (TG) and differential thermogravimetry (DTG) plots are presented in Figure 6.

The organic and aqueous fraction show distinctly different thermal decomposition patterns. The organic fraction has four major peaks with different degrees of overlap in the DTG curves, while the aqueous fraction only shows one major peak at low temperature. The latter indicates the presence of large amounts of highly volatile organics, including water and a limited amounts of higher boiling components.

The solid residue for the organic fraction is much higher (21.6 wt%) than that of the aqueous fraction (4.6 wt%). This supports the idea that the organic fraction contains the higher molecular weight (lignin) components, in agreement with the GPC data.

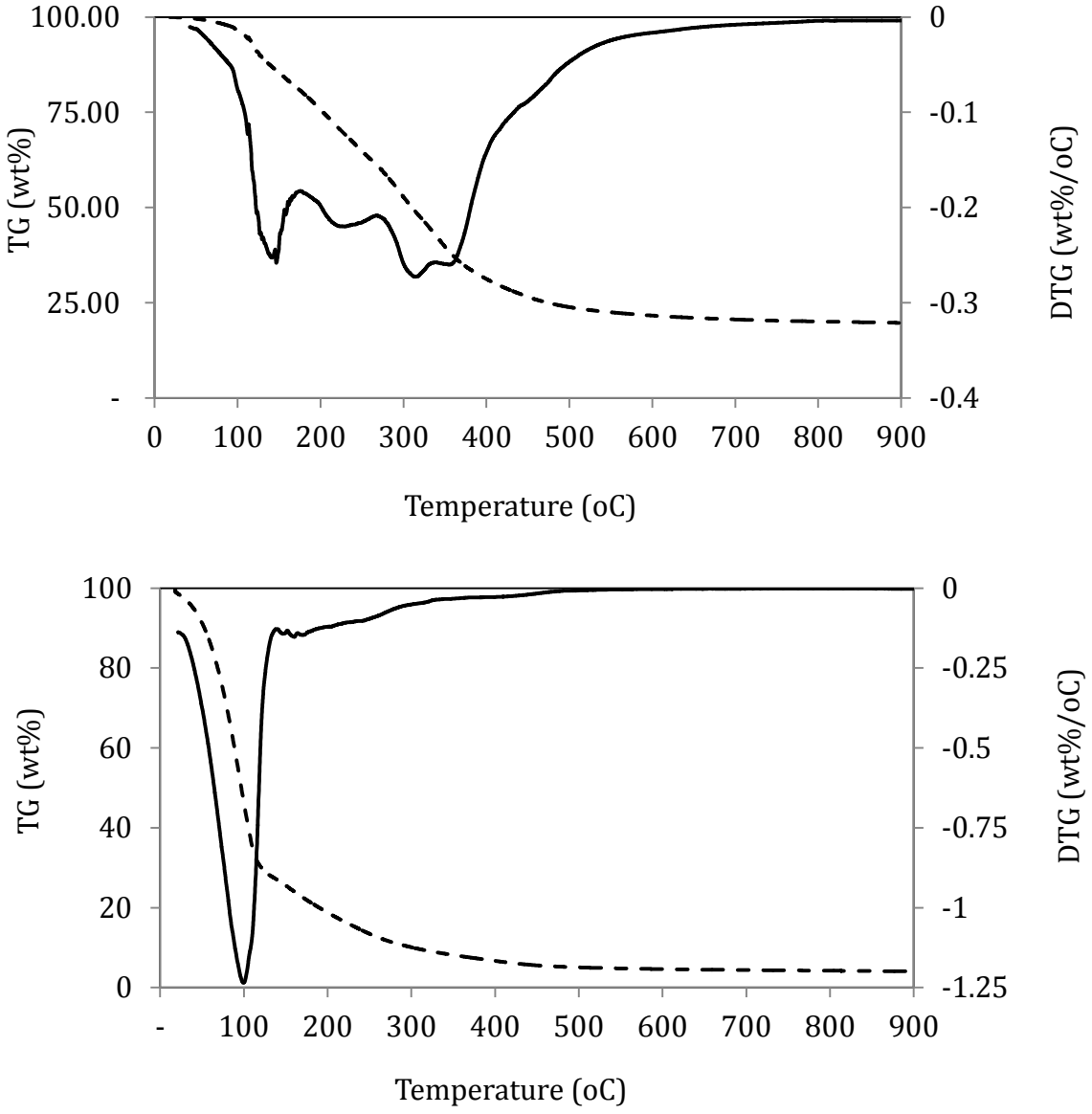

Figure 6. TG/DTG of the organic fraction (upper) and aqueous fraction (bottom) of a liquid product obtained at 507°C

4.3.4. Composition of the off gas

The composition of the gases in the exit during the pyrolysis experiments were determined using an online GC. The gas phase composition in the outlet of condenser 2 (Figure 1) for the three experiments at different pyrolysis temperatures on a N_2 free basis is presented in Table 8. The main gas phase component is CO_2, followed by CO, CH_4 and a mixture of C_2H_4 and C_2H_6. H_2 was below the detection limit of the GC (< 0.5 vol%).

In comparison with pyrolysis experiments using the JCL nut shell as feed, the concentration of CH_4, CO and C2+ is lower than the JCL seed cake while the concentration of CO_2 is much higher.

Table 8. Composition of the non-condensable gases in the outlet of condenser 2

Component	JCL nut shell (vol%) (38)	JCL seed cake (vol%)		
		479°C	491°C	507°C
CH_4	8.9	4.3	5.0	7.0
CO	36.5	20.9	22.0	25.5
CO_2	51.9	73.0	70.8	64.9
C_2H_4	2.6[a]	0.7	0.9	1.2
C_2H_6		1.1	1.2	1.3

[a] sum of C_2H_4 and C_2H_6

On the basis of the product properties and chemical analysis of the two liquid fractions, it may be concluded that the organic fraction contains limited amounts of water (17.15 wt%) and relatively apolar organics. GPC data supported by TGA measurements combined with the observation of a limited amount of volatile GC detectables (11 wt%) indicate the presence of substantial amounts of higher molecular weight components. These can be larger sugar type molecules as well as lignin derived oligomers. The aqueous phase contains substantial amounts of organics (38 wt%, the remainder being water) with a relatively high oxygen content. The amount of higher molecular weight components in this fraction is considerably lower than for organic fraction, as evidenced by GPC measurements and the TGA data. Part of the nitrogen components (mainly proteins) in the DOSC feed ends up in both liquid products and as such contain significant amounts of nitrogen. Based on GC measurements, the majority of the N-containing compounds in the organic phase are not volatile and GC-detectable and likely present in the form of oligomers.

4.4. Conclusions

The pyrolysis of *Jatropha curcas* L. (JCL) seed cake in a continuous bench scale pyrolyzer using rotating cone fast pyrolysis technology at a scale of about 2.5 kg/h was successfully demonstrated. The total runtime for three successive runs was over 7 h and operational issues were not encountered. Spontaneous phase separation of the pyrolysis liquids was obtained after pyrolysis to a relatively apolar organic and a polar aqueous phase. The total liquids yield was between 50 and 55 wt% (daf) at pyrolysis temperatures in the range 479-507°C, the remainder being char (19-21 wt% daf) and gas (16-16 wt% daf). The pyrolysis oils contain relatively large amounts of nitrogen and oxygen. The major constituents are organic acids, phenolics and N containing compounds, the major being acetic acid, 2-furanmethanol, butyrolactone and 2(5H)-furanone.

For the products to be used as a biofuel for stationary or instationary combustion engines, further upgrading is required to meet the fuel standard specifications. Particularly the nitrogen and oxygen content should be reduced considerably. A promising technology for this purpose involves a catalytic

hydrotreatment using supported heterogeneous catalysts and molecular hydrogen. This technology has shown to have high potential for the conversion of fast pyrolysis oils for non-nitrogen biomass feeds to hydrocarbon, drop in biofuels. The catalysts typically used for the removal of oxygen (hydrodeoxygenation) like CoMO and NiMo on alumina are also known to be active for hydrodenitrification and actually these reactions are in general known to be more facile than hydrodeoxygenation. Other product applications involve the separation/isolation of (nitrogen) containing compounds for further upgrading to bulk chemicals followed by the upgrading of the remaining fractions to e.g. a biofuel. These upgrading studies are currently in progress and will be reported in due course.

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Chapter 5

Valorization of *Jatropha curcas* L. plant parts; nut shell conversion to fast pyrolysis oil

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Abstract

The biorefinery concept is a very powerful concept to optimize the conversion of biomass resources to value added products with a minimum loss of energy and mass and a maximum overall value of the production chain. We here report our activities on the application of this concept to valorize the *Jatropha curcas* L. (JCL) shrub, a (sub)-tropical plant producing high quality plant oil that may be converted to biodiesel in good yields. Within a research consortium of Dutch and Indonesian researchers, we are exploring high value added outlets for byproducts of the JCL plant (leaves, latex) and seed processing units (press cake). As an example, we here report fast pyrolysis experiments to convert the nut shells to fast pyrolysis oil, a promising second generation biofuel. The fast pyrolysis experiments were carried out in a continuous bench scale pyrolyzer at a throughput of 2.27 kg/h at 480 °C and atmospheric pressure. The nut shell pyrolysis oil was obtained in 50 wt.% yield, the remainder being char (23 % wt.%), gas (17 wt.%) and ash. Relevant product properties of the oil were determined and indicate that the oil is inhomogeneous in nature.

5.1. Introduction

5.1.1. Possible applications of *Jatropha curcas* L. plant parts and processing residues

The *Jatropha curcas* L. (JCL) plant is currently receiving a great deal of attention [1-3]. JCL has been recognized as a source for a medium viscosity pure plant oil (PPO) that is easily converted to biodiesel with good product properties [4]. Both JCL PPO and biodiesel have been tested successfully in stationary diesel engines [1,5]. The growing global biodiesel market has attracted investors and project developers to consider JCL biodiesel as a substitute for fossil resources to reduce green house gas emissions. The plant appears to have certain advantages compared to other (tropical) oil producing trees and plants. It has been mentioned that JCL is drought resistant and may grow at extreme conditions where other tropical plants and trees like the palm oil tree cannot survive or will produce unacceptable low yields of oil bearing fruits [2]. In addition, the oil is toxic and as such JCL oil does not compete directly with food applications. This is of prime importance as the current first generation biofuels like biodiesel and bioethanol are derived from feedstocks that are also used in the food chain (various grains for bioethanol and pure plant oils for biodiesel). The food versus fuel discussion is still ongoing and puts serious pressure on the public acceptance of first generation biofuels [6]. A recent review expresses that JCL biodiesel certainly has potential but stresses that most claims on yields, simultaneous waste land reclamation capability and environmental impact are not from scientific literature and likely too optimistic [1].

Although the current focus of JCL valorization is mainly on biofuels (PPO and biodiesel derived thereof), the plant produces many other potentially useful products [2]. For instance, the fruit is rich in sugars and could be applied for bio-ethanol production by fermentation [7]. The seed cake, the residue after pressing the oil, may be used as animal feed (after detoxification), as a source of N-containing chemicals [2] or find industrial applications (adhesives) [8]. The fibers may be applied as a binder in construction materials and various parts of the trees contain interesting components with pharmaceutical applications and can be of medicinal value. The shell of the seeds is rich in lignin and may be used for energy generation [3]. An overview of possible applications mentioned in the literature is given in Figure 1.

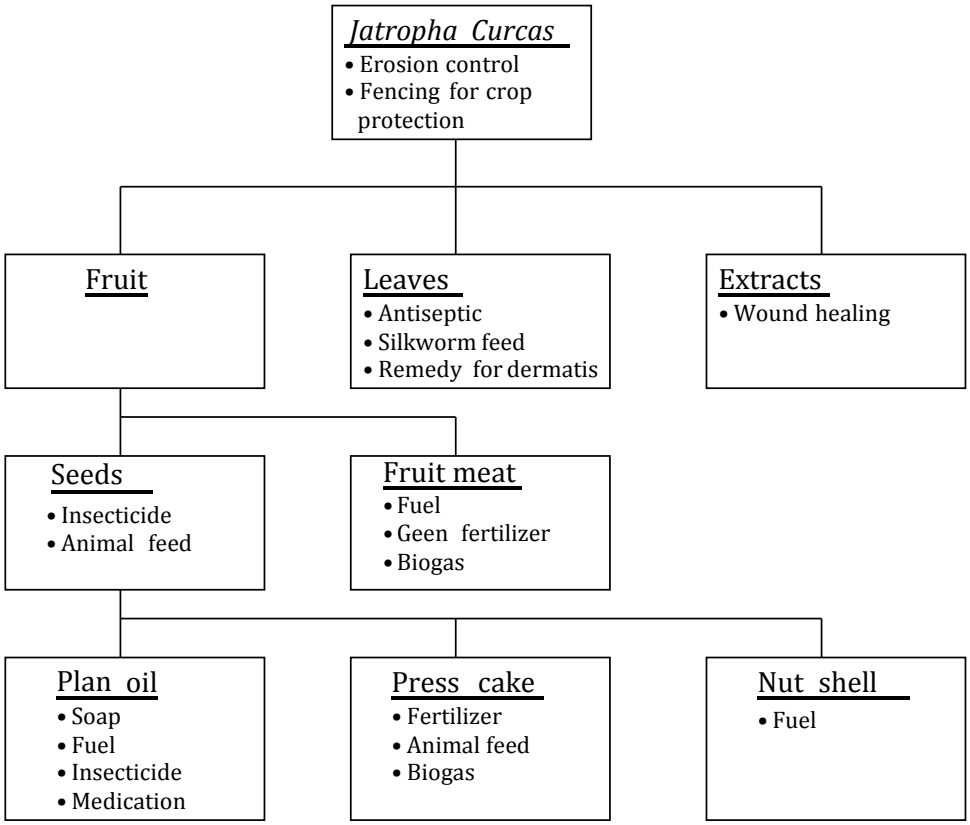

Figure 1. Possible applications of the *Jatropha curcas* L. plant [9]

Evidently, there is a broad range of potential applications, products and associated markets available for the byproducts. Valorization of these products is highly desirable for the following reasons:

- To increase the economic profit of the complete product chain,
- Without byproduct valorization, large amounts of waste products will be produced at the processing units, leading to large negative impacts on the environment.
- The products are made from green, renewable resources and fit with the trend towards the development of bio-based economies

In 2006, a research team consisting of researchers from both Indonesia (Badan Pengkajian dan Penerapan Teknologi and the Institut Teknologi Bandung) and the Netherlands (Wageningen University and Research Center and the University of Groningen) started a 5 year project on the valorization of JCL PPO and the byproducts of the JCL plant using the biorefinery concept. The team consists of 8 PhD students and supporting staff from both the Netherlands and Indonesia. In the following, a short overview of the project will be provided. Subsequently, the research activities aimed at valorization of the nut shells will be given. We will demonstrate that it is possible to convert the lignin rich nut shells into fast pyrolysis oil, which is considered a very attractive second generation biofuel.

5.1.2. The biorefinery concept

Biorefining aims at full valorization of the biomass source by performing the overall processes with a minimum loss of energy and mass [10,11]. It consists of efficient fractionations/conversions of the biomass source into various value-added products and energy using physical separation processes in combination with (bio)-chemical and thermo-chemical conversion steps [11]. Large-scale biorefineries are operational already. Examples are the production of soy oil and soy protein from soy, wheat starch and gluten from wheat and potato starch and protein from potatoes. However, these existing biorefineries produce predominantly food products whereas the JCL biorefinery concept explored by our team has a strong focus on non-food applications. A possible biorefinery scheme for JCL is given in Figure 2.

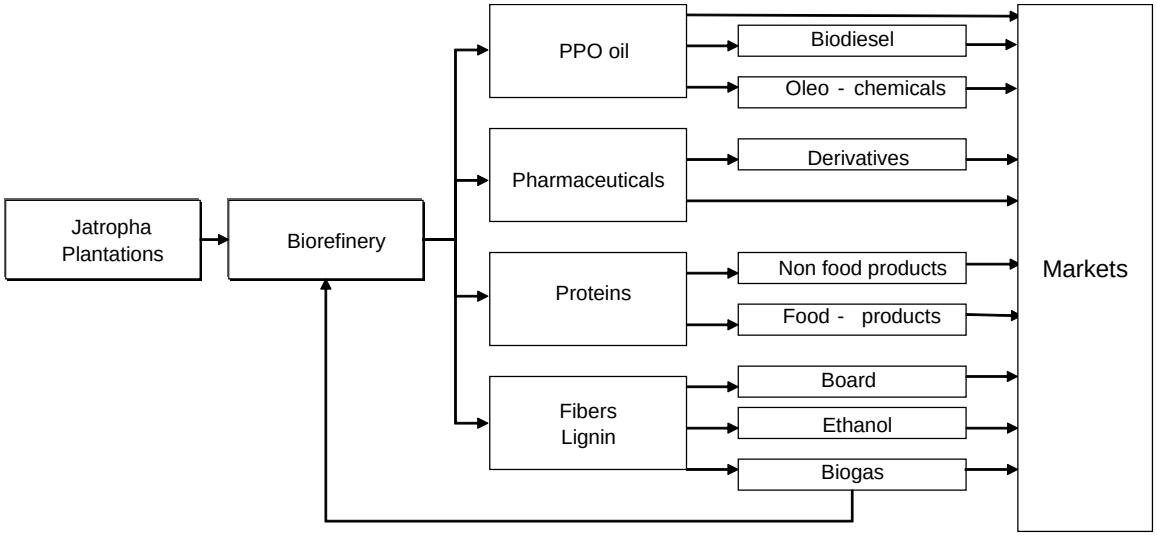

Figure 2. A possible biorefinery concept for JCL (simplified scheme)

Within our Indonesian-Dutch JCL research team, a number of topics to valorize main- and byproducts are covered:

a. Optimisation of the production process for JCL oil

Traditionally, JCL oil is obtained by pressing the seeds of the plant. For a number of applications (for example biofuels), the oil needs further upgrading to meet the often stringent quality criteria. In this subproject, seed pressing technology is optimized, alternative oil recovery procedures are explored (for example enzyme assisted solvent extraction) [12] and process-product performance relations will be established. JCL PPO and the press cake are known to be toxic due to the presence of certain diterpenes and proteins [1,13]. Particular attention will be given to the development of efficient detoxification procedures to allow for safe handling and to increase the value of the byproducts.

b. Development of interesting product outlets of JCL oil

An important and growing outlet for plant oils is the conversion to biodiesel by *trans*-esterification with methanol and a basic catalyst [4]. This leads to improved product properties. For example, the viscosity is reduced considerably which has a positive effect on engine performance. We are exploring alternative catalytic concepts to lower the viscosity of JCL PPO, for example by the application of catalytic metathesis reactions of the PPO with olefinic substrates like ethylene [14].
Natural oils are also important building blocks for the (oleo-) chemical industry [10,11]. Catalytic technology to prepare epoxidized JCL oil is explored within the project. This compound could be an attractive building block for derivatives that may find applications as biolubricants, reactive thermosetting resins and as plasticizers for PVC. In a second project, pharmaceutically interesting compounds from the oil will be identified and their medicinal value and potential to be used as chiral synthons for high value addedpharmaceuticals will be explored.

c. Exploration of attractive technology to valorize byproducts

Byproducts such as the press cake from the seeds, the fruit bodies as well as the leaves of the plant offer additional opportunities for interesting product outlets [2,3]. Examples are the applications of the press cake proteins as a source of animal feed (after detoxification) [15] and/or industrial applications like glues, coatings and films [8]. Improved isolation procedures for protein recovery are explored within the project. The lignin as well as the fibers may be applied for making construction materials whereas the carbohydrates could be applied as a source for bio-ethanol [7]. These topics are also covered within the project.

5.1.3. Fast pyrolysis technology

In this chapter, the use of fast pyrolysis technology to valorize the JCL nut shell is discussed. This paragraph gives some insight in fast pyrolysis technology and product properties of the resulting fast pyrolysis oils. It is not intended as a comprehensive review, for this the reader is referred to recent reviews in the field [16-19]. Fast pyrolysis is a promising conversion technology for lignocellulosic biomass [20]. It is a medium temperature process (400-500°C) in which the biomass feedstock is thermally degraded in the absence of air/oxygen to solids (charcoal), liquids (fast pyrolysis oil) and gaseous products. The fast pyrolysis oil is considered a very attractive second generation biofuel. It has a higher energy density than the solid biomass source and can be transported more easily. Typical liquid product yields are a function of the feedstock, processing conditions and equipment and may be up to 80 wt% on dry biomass. Char (10-20 wt%) and combustible gases (10-30 wt%) are the major byproducts. The char (biochar) is currently receiving a lot of attention as it has good potential for soil improvement [20]. The gas phase generally consists mainly of CO, CO_2 and H_2 and may either be used for energy generation or for the synthesis of (bulk)-chemicals (for example methanol and FT-diesel) [19].

Many different types of pyrolysis reactor configurations have been developed over the last decades [20,22]. Examples include fluidized beds, transported and circulating fluidized beds, spouted beds, ablative and vacuum pyrolysis. Recent developments include microwave assisted pyrolysis [23] and plasma pyrolysis [24].

A process scheme for a typical pyrolysis process is provided in Figure 3. The biomass is fed to the reactor where it is rapidly heated (< 2 s) by hot sand. The vapor phase leaving the pyrolysis reactor is cooled in a quencher with cold fast-pyrolysis oil. The condensable fast pyrolysis liquids are collected. The char and the sand are transported to a combustor, where the char is combusted with air to generate heat for the endothermic pyrolysis process. The hot sand is recycled to the reactor.

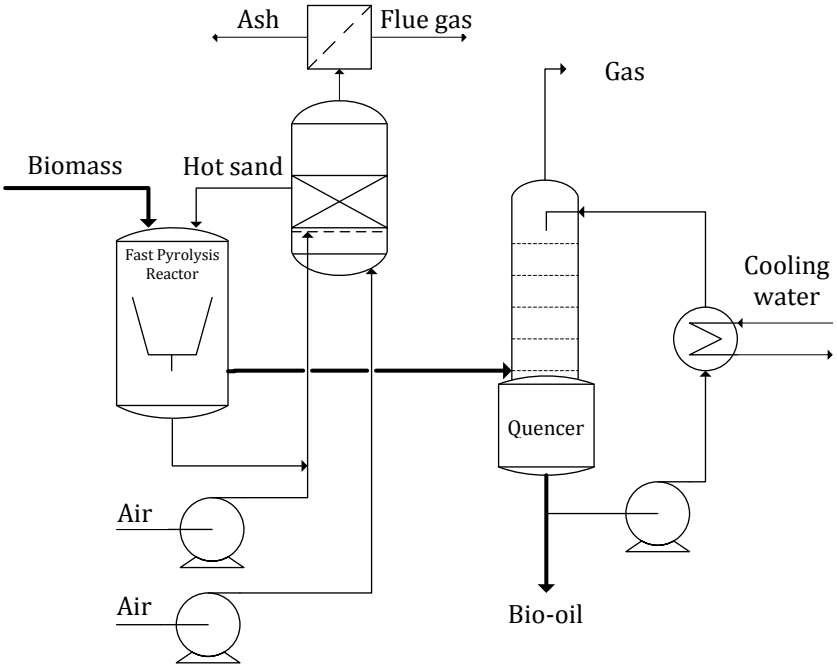

Figure 3. Process flow diagram of BTG's fast pyrolysis process of biomass for pyrolysis oil production (Courtesy of BTG B.V.)

Developments in fast pyrolysis technology have been impressive and the process is now close to full scale commercialization. To the best of our knowledge, the largest two plants constructed to date are a 2000 kg/h unit of BTG/Genting in Sanyen, Malaysia in 2005 [25] and an 8000 kg/h Dynamotive Plant in Canada [20]. The biomass feedstock for the BTG/Genting plant consists of empty fruit bunches from the palm-oil industry. Recently, Dynamotive announced plans for the construction of a 200 ton/day fast pyrolysis plant in the US using saw dust as the feedstock [26].

Fast pyrolysis is a very versatile technology with respect to feedstock and a wide variety of biomass has been pyrolyzed successfully [18]. Examples include residues from the wood industry and agricultural waste products. Waste biomass sources with a high potential include bagasse, rice husk, rice straw, switchgrass, wheat straw and empty fruit bunches of the palm oil industry [27].

To the best of our knowledge, the use of the JCL nut shells as a feedstock for a fast pyrolysis process has not been explored to date. Pyrolysis technology has been applied for valorization of the residue of JCL after oil extraction [28]. This material (press cake) is a mixture of kernel material and shells with residual amounts of PPO. In this case, slow pyrolysis (T = 400-800 °C, hold times > 15 min) was applied with the aim to produce porous char. Activated carbons with high surface areas were subsequently obtained by treatment of the pyrolysis char with concentrated KOH or H_3PO_4. The same group also explored the thermal decomposition characteristic of JCL press cake using thermogravimetric analysis [29]. Effects of heating rate (5-90°C/min), reaction temperature (500-900°C), and hold time at final temperature (3-15 min) on the thermograms, kinetic parameters as well as product distribution were evaluated.

Fast pyrolysis oil, also known as bio-oil, is a dark brown liquid with a pungent odor. The higher heating value (HHV) is about 16-19 MJ/kg, which is about half of crude fossil oil (42 MJ/kg) [20]. However, fast pyrolysis oil contains less ash and is easier to transport than the original solid biomass source. Some important product properties of fast pyrolysis oil are shown in Table 1. The product is rather acidic, contains significant amounts of water and bound oxygen and has a relatively high viscosity. Upon storage, the oil tends to phase separate, although effective measures have been developed to circumvent this issue (for example by alcohol addition) [19].

Table 1. Typical properties of wood derived fast pyrolysis oil [20]

Properties	Typical Value
Water content (wt%)	15-30
pH	2.5
Specific gravity (kg/l)	1.2
Elemental analysis, dry basis (wt%)	
- C	54-58
- H	5.5-7.0
- O (by difference)	35-40
- N	0-0.2
Ash	0-0.2
HHV as produced (25% water content, MJ/kg)	16-19
Viscosity (at 40°C and 25% water, cP)	40-100
Solid (char, wt%)	0.2-1.0

Fast pyrolysis oil contains up to a thousand of different chemical components that may be classified according to functional groups. Typical compound classes are organic acids, aldehydes, ketones, phenolics and alcohols [30].

An immediate application of fast pyrolysis oil is energy generation. Research has been conducted on the use of the oil in boilers, gas turbines and large diesel engines for

electricity generation [20]. Recently, co-feeding of the pyrolysis oil to a gas fired power station of Electrabel in Harculo has been succesfully demonstrated [24]. Pyrolysis is also gaining increasing importance as a pre-treatment step for gasification or combustion processes [17].

Another interesting application is the use of the oil as a source for chemicals. The oil contains various oxygen containing, high value addedcompounds [30]. Examples are hydroxyacetaldehyde (glycolaldehyde), the smallest sugar molecule, acetol and organic acids like acetic acid and formic acid. Levoglucosan is an interesting sugar derivative that can be isolated relatively easily from the oil. The pyrolysis oil contains various low molecular weight phenolics arsing from breakdown of the lignin part of the ligno-cellulosic biomass during pyrolysis. These may find applications in the wood adhesive industry as a (partial) replacement of phenol in phenol-formaldehyde and related resins [11,31].

5.2. Experimental Section

5.2.1. Materials

The JCL seeds were obtained from a plantation near Bandung, Indonesia. The nut shells were manually removed from the seed. The shells were ground in a DFH048 grinder.

5.2.2. Analytical methods

5.2.2.1. Ash content of the nut shells

The nut shells were first dried overnight at 105 °C. Samples of the dried feedstock were then weighed and placed in an oven at 550 °C. After about 8 h the sample was cooled down to room temperature. Before the amount of ash was weighed, the sample was again dried at 105 °C for 24 h to remove any moisture obtained from the air during cooling. The analyses were performed in triplo, which resulted in a relative error below 1%.

5.2.2.2. Elemental composition

The elemental composition of the fast pyrolysis oils and the nut shells (C, H and N) were determined using a Euro Vector 3400 CHN-S analyzer. The oxygen content was determined by difference. The reported values are the average of two independent analyses.

5.2.2.3. Determination of the metal composition of the recycle sand

The metal composition was determined using inductively coupled plasma (ICP). Samples were heated in an oven at 550 °C until they were reduced to ash. The resulting ash was dissolved in a 2 wt% HNO_3 solution and measured by ICP.

5.2.2.4. Determination of the water content of fast pyrolysis oil samples

The water content of the pyrolysis oil samples was determined using a Karl-Fischer titration (702 SM Titrino, Metro-Ohm). The samples were dissolved in Hydranal solvent (Riedel-de-Haen) and titrated using Hydranal Composite 5 (Riedel-de-Haen).

5.2.2.5. NMR analysis

^1H NMR spectra were recorded on a 200 MHz NMR (AMS100, Varian). The samples were dissolved in $CDCl_3$.

5.2.2.6. Viscosity measurements

The viscosity was measured using a Brookfield viscosity meter using spindle RV 6. The viscosity was measured at 22.4 °C for 10 min at a shear rate of 1.67 s^{-1}.

5.2.2.7. pH measurements

The pH of each sample was measured using a 691 pH meter from Metrohm.

5.2.2.8. Flash pyrolysis experiments

Before a pyrolysis experiment, the shells were dried to a moisture content of 4.7 wt% using an electrical oven at 105 °C. The feeding system of the pyrolysis unit was calibrated using the dried JCL shells to determine the pre-determined input feed rate. During these calibration tests the shells were processed through the feeding section, which resulted in grinding of the shells. The average particle size of the shells was thus reduced within the system to an approximate size of 1 mm. The flash pyrolysis experiments of the JCL nut shell were carried out in a continuous flash pyrolyzer with a maximum throughput of 5 kg/h using rotating cone technology (Figure 4).

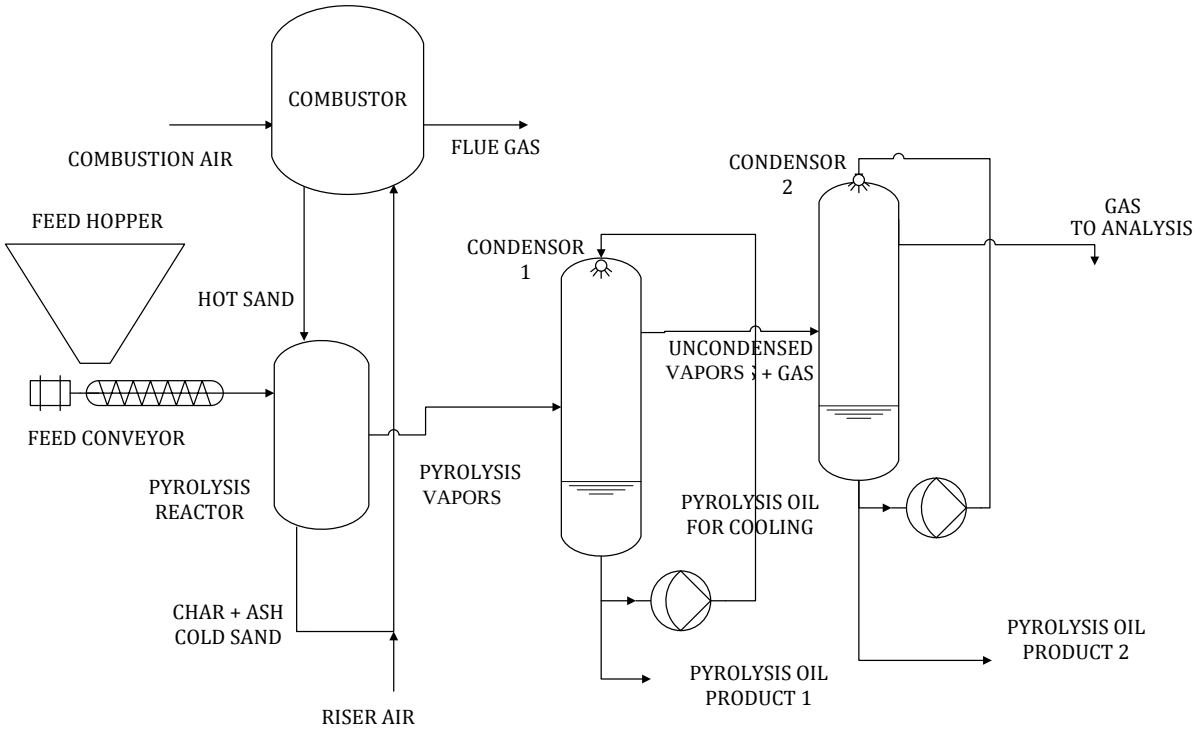

Figure 4. Schematic representation of the bench scale flash pyrolysis set-up used in this study

The experiments were carried out at atmospheric pressure with a typical feeding rate of 2.27 kg/h and a pre-set pyrolyzer temperature of 450 °C. The experiment was run for 80 min. The actual reactor sand in- and outlet temperatures were 492 and 472 °C, respectively. The reactor temperature was higher than the pre-set temperature of 450 °C. This is likely due to the formation of relatively high amounts of char which is known to lead to higher combustion temperatures. The actual combustor temperature was 563°C. The pyrolysis vapors were liquefied in two successive condensers (1 and 2) at temperatures around 40 °C (Figure 4). Cooling was performed by spraying the vapors with cold fast pyrolysis oil. At the start up of the process, both condensers were partly filled with start-up oil, in this case fresh pine wood pyrolysis oil. During the experiments, various oil fractions were collected in both condenser 1 and 2. The fractions were analyzed and weighted for mass balance calculations. The char yield was determined indirectly, because the char is burned inside the combustor to generate the heat required for the endothermic pyrolysis process. The amount of oxygen required for combustion was determined by measuring the oxygen content of the flue gas. Based on the oxygen balance the amount of char which is combusted can be calculated.

5.3. Results and Discussion

The JCL seeds consist of a hard black nut shell and a soft white kernel containing the plant oil in a protein rich matrix. Typically the shells represent about 48 wt% of the total nut [32]. With an estimated nut production of 2 ton/(ha.year) [1] this corresponds to a production of about 1 ton of nut shells per hectare per year. Thus, identification of higher value added outlets for the nut shell is worthwhile and deserves further attention. In the following the chemical composition will be discussed and the application of the nut shells as a feedstock for fast pyrolysis will be explored.

5.3.1. Chemical composition of the nut-shell

The water content and the elemental composition of the nut shells were determined. The water content of the nut shells was 11.0 wt%. This value is close to literature data (8.1-10.2% [13] and 9.1 wt% [33]). Before pyrolysis, the feedstock was oven dried at 105 °C to reduce the moisture content. This facilitates processing and improves the quality of the resulting product oil. The moisture content after drying was 4.7 wt%.

The elemental composition of the nut shells was determined by elemental analysis and the results are given in Table 2. Of interest is the N-content, which is higher than reported in the literature. This difference is likely due to the presence of residual amounts of white kernel material in our samples, which is known to be rich in proteins [13].

Table 2. Elemental composition of the JCL nut shell[a]

	C	H	O	N	S	Ash
This study	50.3	6.6	38.3[b]	1.8	n.d.[c]	3.0
Literature [31]	48.5	5.7	41.0	0.67	<0.01	4.08[d]

[a] in wt% on wet basis; [b] by difference; [c] not determined; [d] by difference

The ash content, an important input parameter for fast pyrolysis, was 3.0 wt%. This value is in line with literature data (2.1-6 wt%, depending on the variety) [13]. Wever *et. al*. also determined the contents of the main constituents (cellulose, hemicellulose and lignin) of the nut shell and found that the shell is relatively rich in lignin (47.6 wt%) [32]. Typically, lignin values for softwood biomass are between 23-33 wt% and 16-25 wt% for hard wood biomass [34]. The values for cellulose and hemi-cellulose were 22.3 and 23.8 wt% respectively. The hemi-cellulose fraction is at the low end for woody biomass (25-35 wt%), whereas the cellulose content is considerably lower than found for woody biomass (40-50 wt%). Thus, it can be concluded that the nut shell is relatively rich in lignin and contains relatively low amounts of cellulose. This is expected to have a profound effect on the composition and properties of the resulting fast pyrolysis oil.

5.3.2. Fast pyrolysis experiments

The fast pyrolysis experiments of the JCL nut shell were carried out in a continuous flash pyrolyzer with a maximum throughput of 5 kg/h using rotating cone technology (Figure 4). An overview of the number and amount of the various oil fractions collected during a representative run is provided in Table 3. The first fraction was highly diluted with the start-up oil and not representative for the JCL nut shell oil.

Table 3. Overview of oil fractions collected during a representative pyrolysis experiment

Pyrolysis-oil details	Condenser 1 (main product)		Condenser 2 (balance closure)	
	Mass [kg]	Moisture [wt%][a]	Mass [kg]	Moisture [wt%][a]
Start-up oil (pine oil)	0.655	22.0	0.3830	22.0
Fraction 1	0.700	28	0.1847	21.7
Fraction 2	0.513	33	0.3422	21.0
Fraction 3	0.833	33	-	-

[a] measured directly after production

Besides the dark brown pyrolysis oil, non-condensable gases and char were produced as well. The mass balance for the complete process is given in Table 4. Mass balance closure is acceptable (93%).

Table 4. Mass balance for the fast pyrolysis process of JCL nut shell

Mass balance	Amount (wt%)
Oil yield	50
Gas yield	17
Char yield	23
Ash 'yield'	3
Balance closure	93

The oil yield was 50 wt%. Typical pyrolysis oil yields are between 40 and 65 wt% on dry feed depending on feedstock composition, process conditions and processing equipment [20]. Thus, the liquid yields obtained for the JCL nut shell are at the low end of the reported values. It is well established that feedstocks high in lignin, such as bark and olive husk, have the tendency to give relatively low oil yields [18]. It should be realized that the experiments reported here are the proof of principle only, and further yield improvements are possible by process optimization (e.g. reactor temperature, particle sizes, heating rates).

5.3.3. Properties and elemental composition of the fast pyrolysis oil, gas and char

5.3.3.1. Fast pyrolysis oil properties and composition

The fast pyrolysis oil was isolated as a dark-brown viscous liquid with a typical pungent odor. Initially the oil was free of visible solid particles, however, after 1 month at storage at 4°C, the formation of a small amount of solid material on the bottom of the storage container was observed. Determination of the water content of the samples resulted in a large spread of values, even within a specific oil fraction (1, 2 and 3 in Table 3). One of the possibilities for this phenomenon is the occurrence of phase separation upon storage and the formation of two discrete liquid phases [30]. However, this was visually not observed. An alternative explanation is the occurrence of concentration gradients within a sample. To proof this hypothesis, fraction 3 (stored for 1 month at 4°C) was allowed to settle for 24 h at room temperature and subsequently samples of the top, middle and bottom part of the container were taken and analyzed (elemental composition, pH, water content, viscosity, ^{1}H NMR). The data are given in Table 5, representative ^{1}H NMR spectra of the various samples are given in Figure 5. The pH value of all samples was 3.3-3.4, indicative for the presence of organic acids. The water content, elemental analysis and ^{1}H NMR spectra clearly show the presence of concentration gradients in the sample and indicate that the pyrolysis oil is inhomogeneous in nature. The analytical data for the top sample suggest that it is rich in pure plant oil. The C and H content are high for typical pyrolysis oil and closer to those found for pure plant oils. An ^{1}H NMR spectrum of the top sample (Figure 5) confirms this statement and shows characteristic resonances of the fatty ester chains of a typical PPO (δ 0.8 ppm (CH_3), δ 1.3 ppm (CH_2), δ 5.4 ppm (C=CH)). The ^{1}H NMR spectrum of the bottom fraction is distinctly different and clear resonances of the fatty acid chains of PPO are absent. Clearly visible are resonances of aldehydes and organic acids (δ 8-10 ppm), aromatic protons (δ 6.4-8 ppm), methoxy groups (δ 3-4.2 ppm) and aliphatic methyl and CH_2 groups (δ 0-2.2 ppm), in line with typical data for pyrolysis oils [35]. On the basis of these analyses, it can be concluded that the oils are inhomogeneous and are likely intermediate between a homogeneous and a fully phase separated oil.

Table 5. Elemental composition and selected product properties of the top, middle and bottom samples taken from fraction 3

Product property	Top sample	Middle sample	Bottom sample
pH	3.3	3.3	3.4
Water content (wt%)	23.3	23.9	55.3
Viscosity (mPa.s)	270	100	30
Elemental composition (wt%)			
- C	65.6	27.8	31.0
- H	9.5	8.8	8.7
- N	0.9	1.0	1.1

The PPO in the oil likely originates from the presence of white kernel material in the nut shell pyrolysis feed due to incomplete manual separation. The white kernel is known to be rich in proteins and pure plant oil. This hypothesis is confirmed by visual observations and elemental analysis on the nut shell pyrolysis feedstock. It shows a higher N content compared to literature data (*vide supra*) and is thus indicative for the presence of proteins arising from residual kernel material.

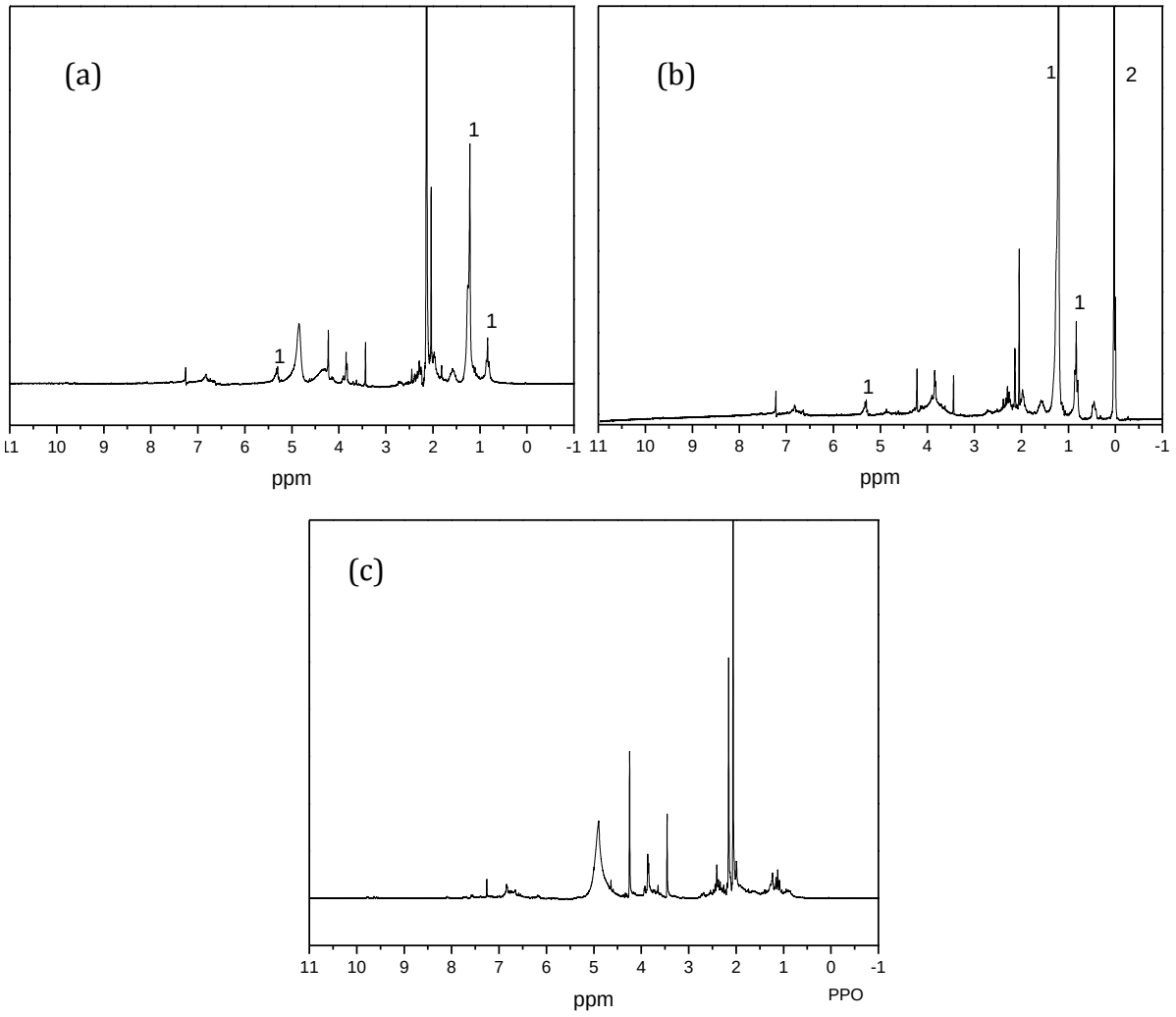

Figure 5. ^{1}H NMR spectra of top (a), middle (b) and bottom (c) sample. 1: main peaks from PPO; 2: internal standard (tetramethylsilane, TMS). Peak at δ 7.21 ppm is from the NMR solvent ($CDCl_3$). All other peaks are from the various components within a typical pyrolysis oil.

5.3.3.2. Composition of the pyrolysis-gas

During the fast pyrolysis process part of the feedstock is transformed into non-condensable gases. The composition of the outlet gases was analyzed with online GC. The composition of the gas in the outlet of condenser 2 (Figure 4) is presented in Table 6. The main component is CO_2, followed by CO and methane. Hydrogen could not be

detected. Furthermore, the gas contains 40 vol% of nitrogen. Nitrogen gas is deliberately fed to the pyrolysis system to act as a purge flow to protect certain instruments. For large scale pyrolysis the amount of nitrogen fed to the pyrolyzer is considerably lower, therefore the gas composition is also recalculated on a nitrogen free basis.

Table 6. Composition of the non-condensable gases in the outlet of condenser 2.

Component	As measured (vol%)	Corrected for N_2 (vol%)
N_2	40.3	0
CO	21.4	36.5
CO_2	30.5	51.9
CH_4	5.2	8.9
C_2+	1.5	2.6

5.3.3.3. Composition of combustor sand and pyrolysis-char

The char produced in the pyrolysis reaction is together with the recycle sand transported from the pyrolysis reactor to the combustor (Figure 4). Here it is burned with an air stream to heat up the sand before it is returned to the pyrolyzer. Thus it is not possible to analyze the composition of the combustor sand and char directly. However, parts of the solids in the combustor are entrained, end up in the off-gas cyclone and may be collected (Figure 4). Analysis shows that the entrained solids contain about 10 wt% unburned char and 90 wt% of ash. The solid fraction was further analyzed by elemental analysis (C, H, N) and ICP. The data are given in Table 7 and 8.

Table 7. CHN analysis of the solids

Element	Amount (wt%)
C	10.8
H	0.58
N	0.47

The ICP analysis indicate that the entrained combustor sand is enriched in metals like Al, Fe, Na, Ca, as well as in P. This confirms that the inorganic ash in the biomass for a large part ends up in the combustor solids and accumulates in the sand recycle in the system. In commercial operation, recycle sand bleeding is required to avoid excessive accumulation of ash in the sand recycle stream. The data clearly indicate that the recycle sand is enriched in important plant nutrients (P, N, Ca, Mg) and has potential to be used as a fertilizer.

Table 8. Metal analysis for entrained and virgin combustor sand

Element	Virgin combustor sand (ppm)	Entrained Combustor sand (ppm)
Al	1440	9100
Fe	340	4420
Na	139	540
Ca	1000	45000
Mg	80	12200
P	<1	11000

5.4. Conclusions and outlook

In this chapter we have provided the proof of principle for the conversion of JCL nut shells by a fast pyrolysis process to pyrolysis oil. The experiments were carried out in a continuous bench scale rotating cone fast pyrolyzer at 470-490°C and atmospheric pressure. The non-optimized pyrolysis oil yield was 50 wt%, the remainder being char (23%) and gases (17%). Relevant properties of the pyrolysis oil were determined. It was demonstrated that the oil is in-homogeneous with both a water and PPO gradient. The PPO likely originates from the presence of residual seed kernel in the nut shell feedstock.

Fast pyrolysis may become an essential element in JCL bio-refineries to valorize the nut shells into fast pyrolysis oil, a promising second generation biofuel. The pyrolysis process is highly flexible in feedstock, implying that other residues (leaves, wood) from the plantations may be valorized as well. The resulting pyrolysis oil may either be used on site for energy generation for example in boilers or transported to larger facilities for further upgrading to for example liquid transportation fuels. Furthermore, the pyrolysis process also produces a char-sand mixture which is rich in minerals and has potential as a soil improver (biochar). The gaseous components may be used for energy generation or bulk chemicals synthesis.

Acknowledgement

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Summary

Important global issues related to the use of fossil resources (security of supply, environmental problems) have stimulated the development of alternative biofuels from renewable feedstocks. Well known examples are bioethanol from sugarcane and biodiesel from plant oils like rapeseed and oil palm. The *Jatropha curcas* L. (JCL) tree has received high attention in the last decade as it produces seeds with a high non-edible oil content and as such can be a source for sustainable biofuels that does not directly compete with food products. Both the JCL pure plant oil and biofuels derived thereof have been tested successfully in diesel engines, and recently also in jet engines. However, the commercialization of JCL biodiesel has slowed down considerably, mainly due to techno-economic issues related to the lower-than-anticipated seed yields. One of the possibilities to improve the economic viability is by giving value to the byproducts by use of the biorefinery concept. This concept aims for full valorization of all by- and waste products into value-added products and as such to maximize the overall value of the JCL chain.

When the JCL seeds are processed for oil recovery, a seed press cake (with or without the seed shells) is obtained as the byproduct. JCL seed cake and seed shells contain considerable amounts of proteins, lignin and cellulose/hemicellulose, besides residual oil. This thesis describes the results of experimental studies on the valorization of JCL seed cake and seed shells. The primary objective of the research was to identify routes for the conversion of JCL seed cake and seed shells into higher added-value products for non-food applications. Only physico- and thermo-chemical processes were explored, biochemical processes were not taken into account.

The potential of JCL seed cake after oil extraction (expelling of seeds followed by a hexane treatment) as a raw material for binderless boards was investigated (Chapter 2). It involves the conversion of the seed cake into boards that can be used as a construction material. The addition of adhesives is not required, since reactive components in the matrix act as internal adhesives. The effects of processing conditions like the water content of the seed cake, pressing temperature, pressure, and heating time on the mechanical properties of the fiber boards were determined and the optimum conditions were a moisture content of 8 wt%, a pressing temperature of 135°C, a pressure of 10 MPa and heating and cooling times of 30 and 15 min, respectively. The mechanical properties of the binderless boards are comparable with typical commercial particle boards obtained with urea-formaldehyde formulations. The effect of the addition of hemp woody core particles on the board properties was evaluated and small clear synergistic effects were observed with an optimum formulation of 50 wt% of hemp.

In the next part, thermochemical processes like catalytic liquefaction and fast pyrolysis were explored to determine their potential to convert the JCL seed cake and shells into value-added products. Experimental studies on the catalytic liquefaction of JCL seed cake are reported in Chapter 3. Different solvents, catalysts and reaction

conditions were tested. Experiments in ethanol gave the highest seed cake conversion and oil yield, both in the presence and absence of a catalyst. The presence of a catalyst in combination with hydrogen has a beneficial effect on oil yield and best results were obtained using a limonite-sulphur catalyst (46 wt% oil, 300°C, 50 bar hydrogen, 30 min reaction time). The oils were characterized in detail using a range of analytical techniques. The liquefied oils have a considerably higher H/C ratio than the feed.

The conversion of JCL seed cake by fast pyrolysis is reported in Chapter 4. The experiments were performed in a continuous bench scale pyrolyzer using rotating cone technology at a scale of about 2.5 kg/h. The pyrolysis oil yield and relevant physical and chemical characteristics (acidity, elemental composition, molecular weight distribution, molecular composition by GC-MS, 2D-GC) were determined. Spontaneous phase separation of the pyrolysis liquids was observed after pyrolysis to an apolar organic and a polar aqueous phase. The total liquids yield was between 50 and 55 wt% (dry ash free basis), the remainder being char (19-21 wt%) and gas (16-16 wt%). The pyrolysis oils contain relatively large amounts of nitrogen and oxygen, and a small amount of sulphur.

Finally, the conversion of the JCL seed shells by fast pyrolysis technology is reported in Chapter 5. The experiments were carried out in a continuous fast pyrolysis unit at 480˚C with a throughput of 2.27 kg seed shells/h. Pyrolysis oil was obtained in 50 wt% yield, the remainder being char (23 wt%), gas (17 wt%) and ash. Relevant product properties of the oil were determined.

Samenvatting

Het gebruik van fossiele grondstoffen zoals olie, gas en kolen staat momenteel onder grote druk vanwege de uitstoot van grote hoeveelheden CO_2 die een rol spelen bij mondiale klimaat veranderingen en het toenemende besef dat het gebruik ervan eindig is. Deze ontwikkelingen hebben gezorgd voor een sterke toename in het gebruik van duurzame energiebronnen voor elektriciteit en warmte opwekking en voor transport brandstoffen. Een bekend voorbeeld is het gebruik van biomassa voor de productie van biobrandstoffen als bio ethanol en biodiesel. Een aantrekkelijke bron voor biodiesel is de olie in de nootjes van de *Jatropha curcas* L. (JCL) struik. Deze olie is niet eetbaar en als zodanig is het gebruik van de olie als biobrandstof niet in directe competitie met voeding. De struik heeft de afgelopen 10 jaar veel aandacht gekregen, mede ook omdat testen lieten zien dat de olie succesvol toegepast kan worden als biobrandstof in diesel en vliegtuig motoren. Echter, de grootschalige markt introductie van Jatropha olie blijft sterk achter bij de verwachtingen, mede als gevolg van lage olieopbrengsten per hectare onder realistische groei condities. Een goede mogelijkheid om de economische aantrekkelijkheid te verhogen is het geven van waarde aan de bijproducten van de olie productie middels het zogenaamde bioraffinage concept. Dit concept heeft tot doel om alle bijproducten van een biomassa gebaseerd productie proces om te zetten in hoogwaardige producten om op deze manier de financiële opbrengst van de totale productie keten te verhogen.

De nootjes van de JCL struik bevatten naast de olie ook een harde schil en een eiwitrijke matrix waarin de olie zich bevindt. Na het verwijderen van de olie blijven de schil en de eiwitrijke matrix (perskoek) over. Dit proefschrift beschrijft experimenteel onderzoek naar mogelijkheden om de perskoek en de schillen om te zetten in producten met een zo hoog mogelijke waarde voor niet voedsel gerelateerde toepassingen. Er is vooral gekeken naar fysische- en thermochemische processen, biotechnologische processen zijn niet in beschouwing genomen.

In hoofdstuk 2 wordt experimenteel onderzoek beschreven naar het gebruik van de JCL perskoek voor het maken van zogenaamde “binderless boards”. Hierbij wordt de perskoek onder druk verhit tot een “board” dat gebruikt kan worden als constructie materiaal in bijvoorbeeld de bouw sector. Voor dit concept zijn geen externe lijmen nodig, reacties in de perskoek bij verhoogde temperatuur zorgen voor de interne vorming van chemische bindingen die het materiaal sterkte geven. Het effect van belangrijke proces variabelen zoals het watergehalte van de perskoek, de perstemperatuur, de persdruk en de perstijd op belangrijke mechanische eigenschappen van het materiaal zijn bepaald. Optimale condities waren een vochtgehalte van 8%, een perstemperatuur van 135˚C, een persdruk van 10 MPa en een perstijd van in totaal 45 minuten. De mechanische eigenschappen van de materialen zijn vergelijkbaar met die van commerciële boards gemaakt met ureum- formaldehyde

lijmen. Daarnaast bleek het toevoegen van hennep vezel een positief effect te hebben op de mechanische eigenschappen van de boards.

Het tweede deel van het proefschrift beschrijft het gebruik van thermochemische processen zoals snelle pyrolyse en katalytische vervloeiing ("catalytic liquefaction") om de JCL perskoek en zaad schillen om te zetten in hogere toegevoegde waarde producten.

Experimentele studies naar de katalytische "liquefaction" van de JCL pers koek worden beschreven in Hoofdstuk 3. Het effect van verschillende oplosmiddelen, katalysatoren en reactie condities op de olie opbrengst, eigenschappen en chemische samenstelling zijn bestudeerd. Het gebruik van ethanol gaf de hoogste perskoek omzetting en olie opbrengst, vooral in de aanwezigheid van een katalysator en waterstof. De hoogste opbrengsten zijn behaald met een limonite katalysator (46% olie, 300°C, 50 bar waterstof, 30 min reactie tijd). De olie is in detail geanalyseerd met een aantal fysisch chemisch en analytische methodes en laat een hogere H/C verhouding zien dan de voeding.

Het gebruik van snelle pyrolyse technologie om de perskoek om te zetten naar een olie wordt beschreven in Hoofdstuk 4. De experimenten zijn uitgevoerd in een continue pyrolyse eenheid, gebruik makend van "rotating cone" technologie op een schaal van ongeveer 2.5 kg/h. De olie opbrengst en relevante olie eigenschappen (zuurgraad, elementaire samenstelling, molecuul gewicht en moleculaire samenstelling met behulp van o.a. GC-MS, 2D-GC) zijn bepaald. De product olie is niet stabiel en spontane fase scheiding in een apolaire organische en polaire water fase werd waargenomen De totale olieopbrengst was ongeveer 50-55% (droge, as vrije basis), daarnaast werden significante hoeveelheden vast residu ("char" 19-21%) en gas (16-16%) gevormd. De pyrolyse olie bevat naast relatief grote hoeveelheden aan stikstof- en zuurstof houdende verbindingen ook kleine hoeveelheden aan zwavelhoudende verbindingen.

In hoofdstuk 5 worden experimenten beschreven waarbij de zaad schillen omgezet zijn naar een olie met behulp van snelle pyrolyse technologie. De experimenten zijn uitgevoerd in een continue snelle pyrolyse opstelling bij 480˚C met een voedingssnelheid van 2.27 kg zaad schillen per uur. De opbrengst aan pyrolyse olie was ongeveer 50%, daarnaast werd ook vast residu (23%) en gas (17%) gevormd. Relevante product eigenschappen van de olie zijn bepaald.

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List of publications

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[2] H. Hidayat, E.R.P. Keijsers, U. Prijanto, J.E.G. van Dam, and H.J. Heeres. *Preparation and Properties of Binderless boards of Jatropha curcas L. seed cake.* Industrial Crops and Products 52(2014) 245-254.

Manuscripts under review

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